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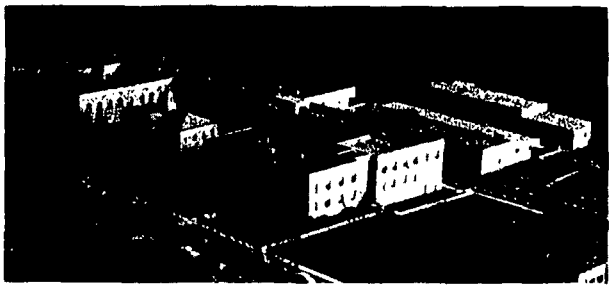

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RESEARCH ON SMELT-WATER REACTIONS

Report Six

to

Advisory Technical Committee

1. Sixth Activity Report of Project Co-ordinator, IPC Project 2419
2. Progress Report of The Babcock & Wilcox Company to June 4, 1965
3. Progress Report of Combustion Engineering, Inc. to June 5, 1965

June 23, 1965

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

SIXTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

June 23, 1965

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In view of the tentative nature of research results and the early stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

SIXTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

This report covers activities of the Project Co-ordinator from March 26 to June 23, 1965. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in the attached reports, covering the period from March 5 to June 5. The Project Co-ordinator visited the Kreisinger Development Laboratory of CE for the Advisory Technical Committee meeting on April 12 and for technical discussion on May 3. A visit was made to the B&W Engineering Department on May 4, and a Chicago meeting was held with B&W research staff on June 22.

The attached report from the B&W Research Center presents a theory based on information from plant explosions, thermodynamic data, calculations, and their study of smelt-water (vapor) reactions. The theory proposes several chemical reactions to account for the exothermic energy release and the generation of combustible gases which may be factors in furnace explosions. Additional laboratory work is planned to develop evidence which should either support the theory or lead to its revision. However, it now seems clear that chemical reactions of pyrolysis of black liquor and of the char-smelt-water system have the possibility of producing combustible gases during emergency situations. The B&W report identifies certain remedial measures which might increase furnace safety, still recognizing that further technical work is necessary in order to justify the responsible recommendation of these practices to the kraft pulping industry.

The attached report from Combustion Engineering significantly advances our concepts of the physical smelt-water explosion. The demonstrations in the spherical pressure vessel of smelt-water explosions taking place in an inert atmosphere prove that explosions of this type do not require oxygen and are not a combustion process. The heat transfer calculations made in an effort to clarify the physical explosion mechanism indicate that the encapsulation concept may be a physical reality, reasonably consistent with our present knowledge of the factors controlling heat transmission under these circumstances. The high-speed motion pictures of laboratory explosions represent a considerable technical accomplishment, and give us further knowledge of the extremely short time factors involved in these explosions. Although we cannot clearly define the mechanism of physical smelt-water explosions, the rather large body of facts now at hand is consistent with the basic concept of a physical explosion initially resulting from encapsulation of water by smelt. It is not surprising, though it is disappointing, to recognize that efforts have been unsuccessful thus far in establishing an additive which could render smelt nonexplosive under furnace conditions. However, there is hope in the possible development of a quenching solution which might be used to flood a furnace on becoming aware of a water emergency.

This research project is receiving specialized assistance from consultants in several areas related to our interests. Dr. Glenn C. Williams, Chemical Engineering Department, Massachusetts Institute of Technology, is contributing from his background in combustion, exotic fuel, and explosion technology. The Explosives Research Center of the U.S. Bureau of Mines has co-operated in plant observations of the three explosions that have occurred in 1965. A contract has been placed with the Structural Research Division, Illinois Institute of Technology Research Center, for structural analysis of the damage from furnace

explosions. From the damage analysis, it is hoped to draw conclusions that will differentiate between combustible gas explosions and direct explosive reactions between smelt and water.

On May 12-16 the Project Co-ordinator visited the pulp mill of Georgia-Pacific Corporation, Crossett, Arkansas, following a recovery furnace explosion on the morning of May 12. The first of a series of three explosions occurred after a blackout, during attempts to light an auxiliary gas burner with a hand torch. It is believed that the first explosion, from ignition of a combustible gas mixture, caused water leaks in the furnace walls and permitted water to reach the smelt bed. The second and third explosions, about twenty seconds apart and three minutes after the first, are believed to have been smelt-water explosions. Evidence for this conclusion are the two localized depressions in the furnace floor and deflections at the lower corner formed by the side and rear furnace walls. Repairs are expected to require about eleven weeks.

The Project Co-ordinator was assisted in the observation of this incident by Dr. G. C. Williams, M.I.T., Mr. J. M. Kuchta, U.S. Bureau of Mines, and Mr. R. R. Robinson, IITRI. Dr. Williams and Mr. Kuchta have expressed the opinion that the two later explosions were caused by a mechanism other than a combustible gas explosion, because the localized damage represented a concentrated release of energy greater than could be realized from the explosion of combustible furnace gas. The Georgia-Pacific management was most co-operative, and the Georgia-Pacific engineering staff obtained a very complete set of deflection measurements for the IITRI structural damage analysis program.

To obtain basic information for the IITRI program, Mr. R. R. Robinson and the Project Co-ordinator visited May 3 at Combustion Engineering, Windsor,

Connecticut, and on May 4 at the B&W Engineering Department, Barberton, Ohio. The first attempt at structure damage analysis will be applied to data from the March 18 explosion at Southwest Forest Industries, Snowflake, Arizona.

On June 4, the Project Co-ordinator visited the mill of S. D. Warren Company, Muskegon, Michigan, where a recovery furnace had been damaged on April 22. Apparently a screen tube failure, directing a blast of steam and water against a panel of the front wall, caused very slight buckstay deflection and loosened insulating material and a casing sheet. Damage was minor and the furnace was restored to service in three days. About two or three minutes after the screen tube failure, there was a second explosion which caused sufficient furnace overpressure to shut down the forced draft fan. It is believed that this explosion resulted from water from the screen tube failure reaching the smelt bed and causing a very light and, therefore, nondestructive smelt-water explosion. Black liquor continued to flow into the blacked out furnace, and may have been effective in cooling the smelt bed so that no further explosions occurred. The facts relating to this incident, as furnished by the mill management, are consistent with our understanding of smelt-water reactions.

Our field observations following recovery furnace explosions have been important in increasing our understanding of the circumstances under which smelt-water reactions take place. Arrangements have been made with CE and B&W for prompt notification to the Project Co-ordinator as soon as an explosion is reported from the field. In the event of a future explosion, it is essential that such notification be made promptly, in order that observation of mill conditions may be started before clean-up operations remove or disturb evidence which may be significant for technical understanding.

In studying recent mill explosions, useful information has been obtained from those furnaces equipped with recorders of oxygen and combustible gas analysis. To add to our knowledge of compositions of furnace atmospheres under emergency or abnormal conditions, the sponsor companies have been asked to loan to the Project Co-ordinator recorder charts from past situations that may be of interest. About eight sets of charts have been received, but no conclusions have been developed from the initial study of these data.

At the April 12 meeting of the Advisory Technical Committee, Mr. W. J. Darmstadt indicated the concern of The Babcock & Wilcox Company regarding the possibility of furnace explosions caused by combustible gas generated by pyrolysis of black liquor used to black out a furnace during an emergency shutdown. He announced company plans to conduct a test program to study the effects of maintaining controlled forced air supply during a shutdown in order to avoid the development of a fuel-rich atmosphere within the furnace. Following the meeting, conversations among various interested individuals resulted in an informal meeting at O'Hare Inn, Chicago, on June 3, arranged by the Project Co-ordinator in collaboration with the Chairman of the Advisory Technical Committee. Babcock & Wilcox and CE were represented and the need was recognized for factual data on furnace conditions during various patterns of shutdown procedures. It was agreed that B&W and CE will each plan and conduct a test program, under their respective responsibilities but recognizing a common interest, on one or more of their recovery furnace installations. Although these are company programs and not formally a part of the Smelt-Water Research Project, the Project Co-ordinator will be kept informed of the test plans, will observe the tests when they are conducted, and will participate in the evaluation and sharing of the test results. The developments are regarded by the Project Co-ordinator as a highly desirable move in the direction of improved shutdown procedures.

In summary, the smelt-water laboratory explosions in an inert atmosphere at Combustion Engineering, and the recent furnace explosion at Crossett have proved that one type of smelt-water explosion involves a mechanism other than a combustible gas explosion. A large body of related facts supports the belief that explosions of this type have a physical mechanism for which the encapsulation of liquid water seems a reasonable explanation. Babcock & Wilcox research has accounted for the presence of hydrogen, carbon monoxide, and pyrolysis products of black liquor which may be present in sufficient volume to result in combustible gas explosions. Babcock & Wilcox research has further led to a theory of noncombustible exothermic energy release from the reaction of water with smelt containing Na_2O. Further work is planned to determine the validity of this theory, and also to determine the possibility of explosions from the presence of elemental sodium.

Our understanding of the smelt-water reactions has significantly increased in recent months. It is now clear that there are at least two possible mechanisms for explosions from smelt-water reactions. One mechanism involves the generation of combustible gases from chemical reaction of the char-smelt-water system, their mixing with air, and subsequent explosive ignition. The other mechanism involves a noncombustible, extremely violent and fast release of energy which appears to rest on a physical mechanism that is not yet completely understood and which is likely to be difficult to prove conclusively in all of its details. The possibility that a noncombustible energy release might result from Na_2O or elemental sodium is still to be determined. Without waiting for the completion of research on explosion mechanisms, we now know enough about possible causes of explosions to justify emphasis on remedial measures, such as more positive control of furnace atmospheres during emergencies either by insuring air-rich conditions, or provisions for establishing an inert atmosphere. Possibilities

for safe and rapid cooling of smelt to temperatures below the explosive range, by flooding with a quenching solution at the onset of an emergency, give hope for reducing the hazard of noncombustible smelt-water explosions. The search continues for an additive to render smelt nonexplosive, but the prospects for success in this area are not encouraging. However, positive elimination of combustible gas explosions is a clear goal toward which we should now move rapidly, while our research on remedies for physical smelt-water explosions is pressed.

THE INSTITUTE OF PAPER CHEMISTRY

Howard S. Gardner

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Co-ordinator, Smelt-Water Research Project
Senior Research Associate
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PROGRESS REPORT

FOR THE PERIOD OF MARCH 5, 1965 TO JUNE 4, 1965

TO

H. S. GARDNER, PROJECT COORDINATOR,
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

July 1, 1965

PROGRESS REPORT OF THE BABCOCK & WILCOX COMPANY ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between March 5, 1965 and June 4, 1965 and the present status of this project. As outlined in our previous reports, our over-all objective is to determine whether and which chemical reactions occur between the smelt-char-combustion gas system that result in explosive reactions with water. A further objective is to determine the thermal decomposition products of black liquor. Having determined these reactions and reaction products, a basis for preventive measures and procedures can be formulated.

During this report period, emphasis was placed on the investigation of smelt-water reactions, both theoretically and experimentally.

SUMMARY OF WORK

1. A theory of a chemical sequence of smelt-water reactions has been formulated. Briefly, this theory states that the reaction of water with sodium carbonate takes place initially in preference to other reactions until sufficient sodium hydroxide has been formed to satisfy the equilibrium constant of the reaction. The subsequent reaction with sodium sulfide then generates hydrogen. If Na_2O is present, its reaction with water takes precedence over the sodium carbonate reaction. If NaOH is present in sufficient quantities to satisfy the sodium carbonate-water reaction, the water immediately reacts with sodium sulfide to generate hydrogen.
2. The smelt-water (vapor) reaction has been investigated experimentally. The significant discoveries were as follows:
   (a) There is an initial time lag, while water is being introduced, during which the smelt takes on water and holds it, and during

which the conversion of water to hydrogen gradually rises to its equilibrium value. This time lag, which we term an induction period, is believed to be the period during which the following reaction takes place,

$$Na_2O + H_2O = 2NaOH$$

(b) The yields of hydrogen after the induction period were much higher than predicted from equilibrium constant and activity calculations.

(c) The graphite crucible interacted with smelt and water vapor and caused the smelt-water reactions to consume 97% of the water added to give a 70% conversion of water to H_2 and a steady-state yield of 55% CO.

(d) Sodium sulfate at a 2.79% level in smelt reduced the maximum conversion of water to hydrogen from 55% to 19%; at the same time the CO_2 level increased from below detection limits to 15%.

(e) When the water vapor additions were discontinued, the smelt continued to give off water, CO, CO_2 and H_2. This release of water was temperature dependent.

(f) No other products, except for slight traces of H_2S, were detected from the reaction of water vapor with smelt.

(g) The effect of higher smelt temperature, although not thoroughly investigated, was to decrease the proportion of hydrogen and increase the proportion of CO and CO_2 evolved.

3. The pressure vessel to be used in carrying out controlled additions of liquid water to molten smelt has been assembled and has undergone preliminary testing.

CONCLUSIONS FROM WORK ACCOMPLISHED TO DATE

As a result of our work to date, as reported in the past and this current progress report, we have come to the following tentative conclusions:

1. Smelt-water, and associated explosions being studied under this program may involve the following factors:
   (a) The thermal decomposition of black liquor can result in large volumes of combustible gas, and the present shut-down procedure can result in a gas-rich mixture that will explode when there is sufficient air in-leakage and an ignition source.
   (b) The reaction of water vapor with smelt has been shown to yield hydrogen and carbon monoxide gas, both of which can be explosive when mixed with air and ignited.
   (c) Molten smelt, after a reaction with water vapor, continues to give off hydrogen and carbon monoxide. This gas evolution reaction may contribute to the observed delay in some furnace explosions involving water.
   (d) Molten smelt absorbs water vapor prior to its reaction to form hydrogen and carbon monoxide. This reaction is tentatively considered to be exothermic.
2. Smelt-water (vapor) reactions release only H_2, CO, and CO_2 gases in significant quantities.
3. The production of H_2 and CO is reduced by the presence of Na_2SO_4 in the smelt. The reduction is approximately proportional to the one-fourth power of the mol ratio Na_2S/Na_2SO_4 in the normal range.

POSSIBILITIES FOR REMEDIAL MEASURES

Our experimental work is continuing and aimed at definitely pinning down the major variables associated with smelt-water reactions. As a result, at this

time we can offer only broad possibilities that are inferred from our work to date. Subject to further work, we feel the following remedial steps may eventually prove desirable.

1. During an emergency shut-down the furnace above the char bed should be kept on the air-rich side.
2. In order to prevent the accumulation of hydrogen and carbon monoxide from smelt-water reactions, it is essential to maintain ignition in the vicinity of the char bed at all times. For this purpose monitored auxiliary fuel burners may be installed and kept on a continuously ignited basis.
3. If it is shown to be in order to prevent the exothermic hydration of smelt, flue gas recirculation and/or steam humidification might be used in the primary air in order that the smelt be continuously maintained in a hydrated state.
4. In order to reduce the amount of hydrogen formed from the sodium sulfide-water reaction, it may be desirable that the salt cake content of the smelt be kept above 3%.

ESSENTIAL WORK TO BE ACCOMPLISHED

Assuming that the smelt-water reactions generate sufficient hydrogen to cause explosions, there remains the question of what proportion of water added to smelt reacts chemically. Therefore we feel it is essential to determine experimentally what the yield from liquid water is, as well as the variables affecting the yield. For example, how is the yield affected by injection of water beneath the smelt vs on top of the smelt?

That smelt takes up water is an important conclusion from our experimental work to date. As this may be an exothermic reaction, work should be carried out

to determine the importance of this reaction in causing explosions. Work should be carried out to answer the following questions:

1. Is this reaction indeed explosive?
2. How is its violence affected by:
   (a) NaOH
   (b) Na_2O
3. Are the results from laboratory-prepared smelts consistent with those obtained from actual furnace smelts?

Suggested preventive measures should also be investigated experimentally. For example, if the results of work now planned show that the exothermic Na_2O-water reaction is of importance, there is a possibility that steam-humidification of primary combustion air would keep the smelt in a hydrated state such as to prevent the exothermic addition of water. This possibility can be explored by determining if smelt will not explode at a certain critical over-pressure of water vapor.

In addition to this work, the question of whether elemental sodium plays a role in the explosion has yet to be resolved. Furthermore, a critical evaluation of the relative effects of the water-gas reaction and the hydrogen production from other sources should be made.

THEORETICAL

In our last progress report we tabulated eighteen reactions that could conceivably take place between smelt and water. In addition to these reactions there are three additional reactions that should be considered:

$$Na_2O + H_2O = 2NaOH \quad (1)$$

$$2NaOH + C = Na_2O + H_2 + CO \quad (2)$$

$$1/4\ Na_2S + CO_2 = 1/4\ Na_2SO_4 + CO \quad (3)$$

The equilibrium constants for these reactions, plotted as a function of temperature,

are shown in Figure 1. For reference purposes, because of their application to the theory of smelt-water reactions discussed below the equilibrium constants for

$$Na_2CO_3 + H_2O = 2NaOH + CO_2 \quad (4)$$

and

$$1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2 \quad (5)$$

are also shown in this figure.

Theory of Smelt-Water Reactions

From a consideration of the equilibrium constants of the possible reactions, and their interaction, we have formulated a theory of the smelt-water reaction and are using it as a guide to our experimental work. This theory is outlined below.

CASE 1 - Smelt containing neither NaOH or Na_2O, over temperature range 1600°F - 2000°F.

1. Initially the predominant reaction takes place between sodium carbonate and water to form CO_2 and sodium hydroxide.

$$Na_2CO_3 + H_2O = 2NaOH + CO_2 \quad (4)$$

While this reaction does not, at first glance, appear to be too favorable, it should be kept in mind that the equilibrium constant expression contains the squared term (a_{NaOH}). At low activities (≈.01) such a term can be shown to effectively drive the reaction to the right.

2. Under equilibrium conditions the CO_2 formed from reaction (4) reacts with sodium sulfide to form CO, and satisfies the CO/CO_2 equilibrium in the following equation:

$$1/4\ Na_2S + CO_2 = 1/4\ Na_2SO_4 + CO \quad (3)$$

At higher temperatures the proportion of CO will increase because of the increasingly favorable equilibrium constant.

3. As the NaOH concentration builds up in the melt, more and more H_2O becomes available to react with sodium sulfide to form H_2.

$$1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2 \quad (5)$$

4. The higher the temperature, because of the increasingly favorable equilibrium constant, reaction (4) predominates to the development of a higher concentration of NaOH. Because of the volatility of sodium hydroxide at 2000°F, it is questionable whether sufficient NaOH can be held in the melt to allow the water-Na_2S reaction, thus lower hydrogen production is to be expected at higher temperatures.

5. The yields of hydrogen and CO are proportional to the fourth root of the activity ratio $\left(\frac{a_{Na_2S}}{a_{Na_2SO_4}}\right)$.

6. After the bulk water has evaporated, the NaOH in the melt decomposes to Na_2O. The water formed then reacts as before (see equations 5 and 3, 4) to form more H_2 and CO.

7. As a corollary, all other reactions tending to form NaOH are suppressed by reaction (4) and will be inconsequential. These include

$$2H_2O + Na_2S = 2NaOH + H_2S$$

$$H_2O + Na_2SO_4 = 2NaOH + SO_2 + 1/2\ O_2$$

CASE 2 - The smelt contains significant amounts of Na_2O or NaOH.

A. Na_2O present

1. In this case the predominant reaction is the reaction of Na_2O with water to give NaOH.

   $Na_2O + H_2O = 2NaOH$

   This reaction is exceedingly exothermic (-44,700 cal/mol of H_2O) and highly favorable.

2. If the amount of Na_2O present forms sufficient NaOH to satisfy the sodium carbonate-water equilibrium, the additional water present will immediately react to form hydrogen from sodium sulfide.

B. NaOH present

1. If NaOH is present in the melt in sufficient amounts to satisfy the Na_2CO_3-water equilibrium, the water will immediately react to form hydrogen.

For illustrative purposes, consider a smelt of the following composition by wt:

75.00%	Na_2CO_3
24.45%	Na_2S
0.05%	Na_2SO_4
.00	NaOH
.00	Na_2O

The question to be answered is what happens when such a smelt reacts with water. We shall attempt to answer this question.

Assumptions

Assume the following equilibrium constants:

$$Na_2CO_3 + H_2O = 2NaOH + CO_2 \qquad K_{1600} = 4.8 \times 10^{-4}$$
$$K_{2000} = 3.5 \times 10^{-3}$$

$$1/4\ Na_2S + CO_2 = 1/4\ Na_2SO_4 + CO \qquad K_{1600} = 4.5 \times 10^{-2}$$
$$K_{2000} = 1 \times 10^{-1}$$

$$1/4\ Na_2S + H_2O = 1/4\ Na_2SO_4 + H_2 \qquad K_{1600} = 4.5 \times 10^{-2}$$
$$K_{2000} = 5.5 \times 10^{-2}$$

Assume the activities of NaOH and Na_2SO_4 are equal to their mol fractions in the melt, and that the activities of Na_2S and Na_2CO_3 follow the equations derived by Rosen[1] from melting point data. These equations are

$$\ln f_{Na_2S} = \frac{3750}{RT} \cdot n^2_{Na_2CO_3}$$

and $$\ln f_{Na_2CO_3} = \frac{3750}{RT} \cdot n^2_{Na_2S}$$

where f = activity coefficient

n = mol fraction

and activity = a = f.n

This gives at 1600°F $f_{Na_2S} = 2.21$ and $f_{Na_2CO_3} = 1.18$ and at 2000°F $f_{Na_2S} = 1.93$ and $f_{Na_2CO_3} = 1.15$. Converting wt % composition to mol fractions, and using these activity coefficients, at 1600° $a_{Na_2S} = .69$, $a_{Na_2CO_3} = .81$ and at 2000° $a_{Na_2S} = .60$, $a_{Na_2CO_3} = .78$.

Assume further that we are interested primarily in gaseous reaction products and that $P_{H_2O} + P_{CO_2} + P_{CO} + P_{H_2} = 1$ atm, or = 100%. Together with this equation the equations to be solved simultaneously become,

$$K_1 = \frac{a^2_{NaOH}}{a_{Na_2CO_3}} \times \frac{P_{CO_2}}{P_{H_2O}}$$

$$K_2 = \frac{a^{1/4}_{Na_2SO_4}}{a^{1/4}_{Na_2S}} \times \frac{P_{CO}}{P_{CO_2}}$$

$$K_3 = \frac{a^{1/4}_{Na_2SO_4}}{a^{1/4}_{Na_2S}} \times \frac{P_{H_2}}{P_{H_2O}}$$

These equations become manageable by hand calculation if the concentration of NaOH is chosen as an independent variable, and furthermore if the Na_2SO_4 concentration is assumed constant. This latter assumption does not lead to serious errors because of stoichiometry, requiring 4 mols of water or CO_2 to form 1 mol of Na_2SO_4, and the associated dependence of the hydrogen and CO yield on the one-fourth root of the Na_2SO_4 activity.

Taking NaOH = .001, .01, .02, .05 and .1 mols per mol of Na_2CO_3, the partial pressures of CO_2, CO, H_2 and H_2O can be determined.

Figure 2 shows a plot of the concentrations (%) expected as a function of mols NaOH/mol Na_2CO_3, at 1600°F and 2000°F. For the sake of clarity the

concentration of H_2O has been omitted. This figure shows graphically how the composition of gases is dependent upon (a) NaOH concentration and (b) temperature. It should be noted particularly that the primary reaction products at low NaOH concentrations are CO_2 and CO; at 1600° the CO_2/CO ratio is much greater than at 2000°. Furthermore, at 1600°, the formation of significant amounts of hydrogen takes place at a much lower NaOH concentration than at 2000°.

Effect of Na_2O

If Na_2O is present, there will be an initial tendency to react exothermically with water.

$$Na_2O + H_2O = 2NaOH$$

Although the equilibrium is most favorable for the formation of NaOH, it must be kept in mind that as NaOH builds up in concentration there will be a decreased tendency for the reaction to take place, and thus gradually water becomes available for the other reactions as shown in Figure 2.

Application of the Theory

The theory outlined above, while admittedly lacking in some details, nevertheless is valuable in several respects.

In the first place, it accounts for the observed delay in some furnace explosions involving water that has been observed. This is apparently the time required to form NaOH in sufficient quantities so that the water is available for H_2 formation. This delay also explains how the explosive amounts of hydrogen are formed in spite of the large excess of water vapor, for the initial reaction is the volatilization of water and the reaction to form CO_2. These non-reactive gases will tend to quench any burning; the delayed build-up of hydrogen then can mix with air to form an explosive mixture. It further explains the observation that at 2000°F apparently the smelt is not explosive, for at this temperature the

major reaction is the Na_2CO_3-water reaction and this equilibrium requires the development of a higher concentration of NaOH.

A further application of the theory would indicate that the injection of water beneath the smelt surface would be more conducive to explosions because the CO_2, formed initially, would have a longer period of time, and therefore a better chance to react with Na_2S to form CO (Reaction 3). On the other hand, water placed on top of the smelt would form CO_2 and CO_2 would tend to escape and not react further.

That green liquor additions to smelt are more reactive is an observation that has been made by different investigators and can be accepted as a confirmed fact. This theory explains such an observation on the basis that the green liquor contains sufficient sodium hydroxide to satisfy the Na_2CO_3-H_2O reaction, and the water is immediately available to form hydrogen from the Na_2S.

In the B&W experiments of several years ago, some smelts gave several explosions at 15-30 second intervals, and in furnace explosions, delayed explosions also have been noted. These delayed explosions can be explained on the basis of the initial formation of sodium hydroxide and its subsequent relatively slow decomposition to water and Na_2O. The water then forms hydrogen from Na_2S which gradually builds up to an explosive mixture in air.

Contribution of Na_2O

It has been stated previously that the reaction

$$Na_2O + H_2O = 2NaOH$$

is a highly exothermic reaction and highly favorable. If, indeed, Na_2O is present in smelts it would be expected to react with water, even in an inert atmosphere, with a violence proportional to its concentration. It is pertinent, then, to examine whether Na_2O would be expected to be present and its possible contribution to observed explosions.

When the standard analysis of smelt is carried out, Na_2O would show up as NaOH and be indistinguishable from it. While the analysis for NaOH in smelt is relatively inaccurate, nevertheless many smelt analyses show the presence of 1-2% NaOH, and therefore we conclude that Na_2O or NaOH may indeed exist in some smelt beds.

If NaOH is present, it reacts fairly readily with carbon to form Na_2O.

$$2NaOH + C = Na_2O + CO + H_2$$

It therefore appears probable that small amounts of Na_2O exist in a smelt.

Laboratory-prepared smelts, on the other hand, may contain larger amounts of Na_2O, as we will show in the experimental part of this report. Even if great caution is used in preparing anhydrous Na_2S it is most difficult to prevent the formation of NaOH from the hydrolysis of Na_2S.

$$Na_2S + 2H_2O = 2NaOH + H_2S$$

If hydrated material is used for making synthetic smelts, the additional water would be expected to react with Na_2CO_3 to form additional NaOH.

When such smelts are heated in a graphite crucible, as we will indicate later, large amounts of CO and H_2 are liberated. This evolution is interpreted to be a result of the NaOH-carbon reaction noted above. Therefore it is probable that the laboratory smelts contain significant amounts of Na_2O and this must be kept in mind in interpreting experiments based on synthetic smelts.

EXPERIMENTAL

Although our previous reports have indicated that sodium sulfide reacts with water to form hydrogen, and the equilibrium constants for the reaction at 1100-1400°F had been determined, there remained the question of how much hydrogen would form in a molten sodium sulfide-sodium carbonate mixture. Since theory would predict that the yield of hydrogen would be affected by the sodium sulfate concentration, and furthermore, that there should be an induction period for the

reaction, it was important to investigate, on as quantitative a basis as possible, the reaction products and characteristics of the smelt-water reactions. During this report period our experimental effort has been concentrated toward the determination of the course of the reaction. In order to determine these reaction products readily, without the hazards and extraneous effects of explosions, the reaction has been studied by reacting known, measured, amounts of water vapor in an inert carrier with molten synthetic smelt.

Apparatus

A diagram of the experimental apparatus is shown in Figure 3. It consisted of a reaction pot, containing a crucible of 304 stainless steel (graphite has also been used). This crucible held the charge of smelt. Inert gas (helium, or argon) at a fixed rate flowed through a two-step water bubbler at a fixed temperature, via a catch-pot, into the stainless steel bubbler inserted in the molten smelt. The outlet gases were analyzed for water content by Dehydrite absorption and for the other gases by a gas chromatograph. The pressure in the vessel was monitored with a mercury manometer and the exact flow of gas was measured with a wet test meter. A thermocouple indicated the melt temperature.

Procedure

Anhydrous sodium sulfide, prepared as described in Progress Report No. 2, (but by analysis containing 2.0% NaOH) and anhydrous sodium carbonate were charged into the reaction vessel and heated under an inert atmosphere (helium or argon) at 1300° overnight. The total charge varied from 374-554 grams total. At the beginning of the test the temperature was raised gradually, under an inert gas flow atmosphere, and gas analyses made. In general, it was observed that relatively large amounts of hydrogen and CO were liberated and at the same time water was given off. The melt was kept at the test temperature until

the hydrogen and CO content of the exit gas were reduced to below 0.1%. The flow of inert gas (0.5 liters/min) was then started through the water bubbler, the wet test meter read, and the analyses of the gas initially carried out at 10-15 minute intervals. The Dehydrite bulb was weighed at longer intervals (1-2 hrs). The water added amounted to approximately .2 gms/100 gms smelt per hour. The exact amount was, of course, determined from the temperature of the water bubbler and the measured flow. The test was continued until the gas analysis was relatively constant with time (constant for at least 2 hrs). Shut-down procedures were variable, and designed to determine the effect of time and temperature on the reactions taking place after water vapor addition was discontinued.

Results

Three successful runs have been completed, all at a Na_2S level of 25 wt% and at 1600°. The effect of carbon was determined by carrying out the experiment in a graphite crucible. Two levels of Na_2SO_4 have been investigated, one at .01%, the other at 2.79%. In both cases these were the levels determined by analysis at the conclusion of the run. Two unsuccessful runs (3 and 4) were terminated prior to reaching equilibrium.

Run 1 - Graphite Crucible. The results of the first successful run, in argon and using a graphite crucible, 25% Na_2S - 75% Na_2CO_3, are plotted in Figure 4. During the initial phase of the run, before water vapor had been added, relatively large amounts of H_2 and CO were detected at 1600°, with the amounts increasing at higher temperature. This was interpreted to be the result of the NaOH-carbon reaction mentioned earlier. It will be noted that the CO level followed a somewhat erratic pattern, finally levelling off at about 53%, but the hydrogen concentration increased regularly with time until it reached a value equivalent to 70% of the water vapor added. Thus the yield of CO was greater than the theoretical con-

version from the water added. This was interpreted to be the result of a reaction of CO_2 with the graphite crucible to form two moles of CO for each mole of CO_2. The amount of CO_2 present was below the detection limit of the gas chromatograph. In this run only a trace of water in the dehydrite bulb was found, amounting to about 3% of the total water introduced, showing nearly a complete reaction with the smelt under these conditions. As theory predicts, there was an induction period, in this case about 2 hours, during which the hydrogen yield gradually increased to its steady state value. A mass spectrometric analysis of the gas showed only the presence of CO, CO_2 and hydrogen. Traces of H_2S were detected by its odor, but were below detection limits by gas chromatography.

Run 2 - (.01% Na_2SO_4, Stainless Steel Crucible). Because of the serious interaction of the graphite crucible with smelt and water vapor, all additional runs were made in stainless steel crucibles. Some corrosive attack was noted and amounted to the dissolution of 2.5 gms of Fe per 100 gms of smelt. Such corrosion could occur by several mechanisms, (1) attack by Na_2S, (2) oxidation by CO_2 and subsequent solution in the smelt, and (3) attack by NaOH. Because of the predominance of the Na_2S and Na_2CO_3, the first two mechanisms appear most probable and would not alter our conclusions significantly. Although the possibility of the sodium hydroxide-iron reaction has been considered, it is felt that, at the NaOH level involved (0.5%), its contribution would be insignificant.

The results of the run are shown in Figure 5. This run showed, again, the expected induction period before the hydrogen level reaches its maximum value, and the CO level was relatively constant. CO_2 was not detected in this run.

There were several significant features to be noted in this run. Most noticeable and of especial importance was the unexpectedly high conversion of water vapor to hydrogen (55%) after the induction period, this was approximately

two times the amount predicted from the calculation of the equilibrium composition. At the same time, the CO_2 conversion to CO was greater than expected (although it could not be quantitatively determined because of the sensitivity limitations of the CO_2 analysis).

Another significant feature of this run was that it showed that smelt is capable of taking on water and holding it until the water vapor partial pressure was removed. As all of the water introduced, all of the reaction products, and the unreacted water vapor were measured, a mass balance can be made on the water. (This was not possible on Run 1 because of the uncertainty involved with the interaction of the graphite with the smelt.) Of the 2.11 gms of water added/100 gms of smelt, .518 gms/100 gms could not be accounted for and must have remained in the melt. Of this .518 gms, .46 gms, or 88% was absorbed during the addition of the first .91 gms of water (the rest of the water reacted to form CO and H_2).

A further feature of this run was the finding that the smelt continued to give off water and hydrogen long after the water vapor addition had been ended. Figure 6 shows the partial pressure of hydrogen and water exerted by the smelt over a 5-hour period. After holding the melt at 1600°F for approximately 4 hours, the furnace was turned off, inert sweep gas maintained, and the hydrogen level monitored as a function of temperature. As might be expected, the hydrogen content became lower at the lower temperature.

Run 5 - (2.79% Na_2SO_4, Stainless Steel Crucible). We have mentioned previously that the presence of sodium sulfate should tend to reduce the amount of hydrogen formed from the sodium sulfide-water reaction. Hence, if the production of hydrogen can be considered to be a major cause of explosions, some of the hazard could be reduced if it could be shown that small amounts of Na_2SO_4 are effective in reducing the hydrogen production.

In order to determine its effect, 5% Na_2SO_4 was added to a smelt such that the initial starting composition was 5% Na_2SO_4, 25% Na_2S and 70% Na_2CO_3. Upon

analysis at the end of the run we found 2.79% Na_2SO_4. As the stainless steel was more severely attacked, and since it is known that molten Na_2SO_4 is a strong oxidizing agent, it was probable that some of the sodium sulfate was used up in oxidizing the steel. Fortunately, the effect of Na_2SO_4 is approximately proportional to its mol concentration to the 1/4 power and thus its effect is not sensitive to small absolute changes in this concentration range. (At very low concentrations this is not true.)

The results of this run carried out in the same manner as Run No. 2 and shown in Figure 7, indeed show that the hydrogen production was markedly reduced. In the first place, no hydrogen was detected while the melt was held at 1600° and undergoing dehydration. Furthermore, no hydrogen was detected for the first 2 hours after the addition of the water vapor. After the induction period, now considered to be characteristic of the smelt-water (vapor) reactions, the hydrogen yield rose to a maximum 19%, then fell off slightly. As would be predicted from equilibrium considerations of the CO_2-Na_2S reaction, the presence of sodium sulfate also caused a decrease in the production of CO and a corresponding increase in the CO_2.

It was observed from the water mass balance that .57 gms/100 gms smelt was apparently retained in the smelt. This is a reasonable check with the .518 gms/100 gms retained during Run No. 2. Thus it appears that the sodium sulfate had no effect on the water retention during induction period.

The reactions taking place after the addition of water was discontinued were monitored with two different purposes in mind. One purpose was to determine the dependence of the reaction on the amount of water remaining in the smelt; the second purpose was to determine the gas composition as a function of temperature. In order to do this, the temperature was immediately raised to 1700°F and the gas composition determined (including water vapor). The reactor was then shut down overnight and the reaction products determined from 1500-1800° upon start-up the

next day. Thus the products at 1700° were determined initially, and again after the loss of a known amount of water. On an absolute basis, the following table gives a comparison of compositions:

	Initial Run (1700°)	Final Run (1700°)
Amt. H_2O in Smelt	.52 gms/100 gms	.29 gms/100 gms
Percent of Gas (in helium)		
H_2O	2.74%	0.62%
H_2	1.09	.36
CO	.56	.33
CO_2	1.87	.83

The conclusion to be drawn is that the amount of water and other gases evolved appears to be a function of the amount of water retained in the smelt. It will be noted that the ratios of the amount of each component are relatively constant.

An indication of the relative amounts of each constituent in equilibrium with the smelt as a function of temperature was obtained from the analyses carried out at 1500°-1800°F. Placing the total gas (less helium) on a 100% basis, the composition is shown as a function of temperature in Figure 8. These analyses show an increase in CO_2 and CO and a decrease of H_2 with temperature as would be predicted from equilibrium considerations and tend to further confirm our theory of smelt-water reactions.

Discussion and Significance of Results

Yield of Hydrogen. It is highly significant that the yields of hydrogen from the smelt-water (vapor) reaction are as high as were observed, for this dispels any doubt that large amounts of hydrogen can be generated from the smelt-water (vapor) reactions and this should be considered in the smelt-water explosion mechanism. These high hydrogen yields reflect either a more highly favorable equilibrium constant, or a much higher activity coefficient of Na_2S

than has previously been estimated.

In spite of our lack of equilibrium data, the experimental data can be treated quantitatively if we define a conversion factor, $\frac{P_{H_2}}{P_{H_2O}}$, which can be considered to be a pseudo-equilibrium constant at the temperature studied. These factors have been calculated from our steady state data on the three runs described above and are shown in Table I.

Effect of Na_2SO_4. Theory would predict that small amounts of sodium sulfate would reduce the conversion of water to hydrogen as well as the conversion of CO_2 to CO. Before our smelt experiments had been carried out it was hoped that the amounts of explosive gas that could be generated might be reduced to negligible proportions if 2-3% Na_2SO_4 were always present in the smelt. While the goal was apparently not realized, nevertheless it does appear that sodium sulfate does indeed reduce the amount of hydrogen and CO generated from smelt-water (vapor) reactions. Hence, if such gases are found to play a significant role in the smelt-water explosion mechanism, the practice of keeping the salt-cake content at 2-3% could conceivably reduce the magnitude of such an explosion.

The conversion factors, defined above, serve a useful purpose in correlating the data obtained at the two sodium sulfate concentrations. Thus, theory tells us that the conversion factors should be proportional to the fourth root of the mol ratios of Na_2S/Na_2SO_4. In order to test the proportionality factor, the ratio of the conversion factors actually obtained is compared to that calculated from the mol ratios in Table II. It will be noted that the agreement, 4.5 actual vs 4.2 predicted, is reasonably good, and thus it would be expected that the conversion factor could be predicted at other Na_2S/Na_2SO_4 ratios.

Hydration of Smelt. We feel that we have demonstrated conclusively that synthetic smelt takes up significant amounts of water (as water). (We emphasize

that the smelts investigated to date have been laboratory prepared.) The characteristics of such water absorption are such that it takes on water (at least at 1600°) under a partial pressure of water vapor of 30 mm Hg, and releases the water when the over pressure is removed. Furthermore, this release has been shown to be temperature dependent, releasing more at higher temperatures and less at lower temperatures.

It is this temperature dependence that is the feature of importance, for this characteristic shows that if a chemical reaction is taking place, such a chemical reaction is exothermic in character. Such an inference would follow from the observation that the smelt-water hydration is more favorable at low temperatures than at high temperatures.

At the present time we have no direct measure of the heat release and can only consider what alternative mechanisms might cause the smelt to pick up water. We can suggest at least two possible chemical reactions and one possible physical reaction:

(1) A chemical reaction between Na_2O and water to form NaOH.

(2) A hydrate formation of "smelt hydrate" - a chemical combination of unknown composition.

(3) A solubility of water in smelt.

While water solubility in molten materials at high temperatures at first glance appears to be unlikely, nevertheless it has been observed in steel slags, glass and molten salts. Therefore it is possible that this type of physical reaction could take place and such a reaction would not be expected to be highly exothermic.

One could postulate the formation of a hydrated smelt of unknown composition that would exhibit the characteristics that we have observed. Thus the formation of the "smelt-hydrate" would be accompanied by a heat of hydration,

the magnitude of which is unknown.

If sodium hydroxide is present in the smelt it would seem that, in an inert atmosphere, the following reaction would tend to take place.

$$2NaOH = Na_2O + H_2O$$

This would be an equilibrium reaction tending to go to the right so long as water was removed.

Having removed the bulk of the water, upon addition of water, the reverse of the above reaction would take place. This reverse reaction is known to be exothermic (44,000 cal/mol of water reacted).

In our actual experiments, the sodium hydroxide content of the smelt was approximately 0.5% because of the sodium hydroxide content of the Na_2S used. As we had not foreseen the importance of making a water balance during the time the melt was being brought up to temperature, no quantitative values of water evolved during this period were obtained. As a result, we can only postulate that NaOH may have dehydrated to Na_2O prior to the start of the run.

If such a dehydration reaction indeed takes place at 1600°, it would be expected to proceed more favorably at 2000°. After dehydration at the high temperature the exothermic reaction

$$Na_2O + H_2O = 2NaOH$$

would readily take place at a lower temperature. We feel that such a reaction is a distinct possibility and future experiments are aimed at proving its importance to the smelt-water explosion phenomenon.

REACTION OF LIQUID WATER WITH SMELT

Although the chemical reactions expected to take place with liquid water are the same as those shown to take place with water vapor, there is the question of how much liquid water is vaporized by the hot smelt and how much reacts.

A cost control chart showing actual and anticipated expenditures is attached.

Submitted by: C. H. Anderson

Approved by: W. A. Keilbaugh

CHA:vlr

REFERENCES

(1) Rosén, Erik, and Sillén, Lars Gunnar, Acta Chemica Scandinavica, 14, 692-696 (1960).

(2) JANAF Interim Thermochemical Tables, Dow Chemical Co., Midland, Michigan. Sept. 30, 1963.

TABLE I

CONVERSION FACTORS $\left(\frac{P_{H_2}}{P_{H_2O}}\right)$ FOR

SMELT-WATER REACTION (1600°F)

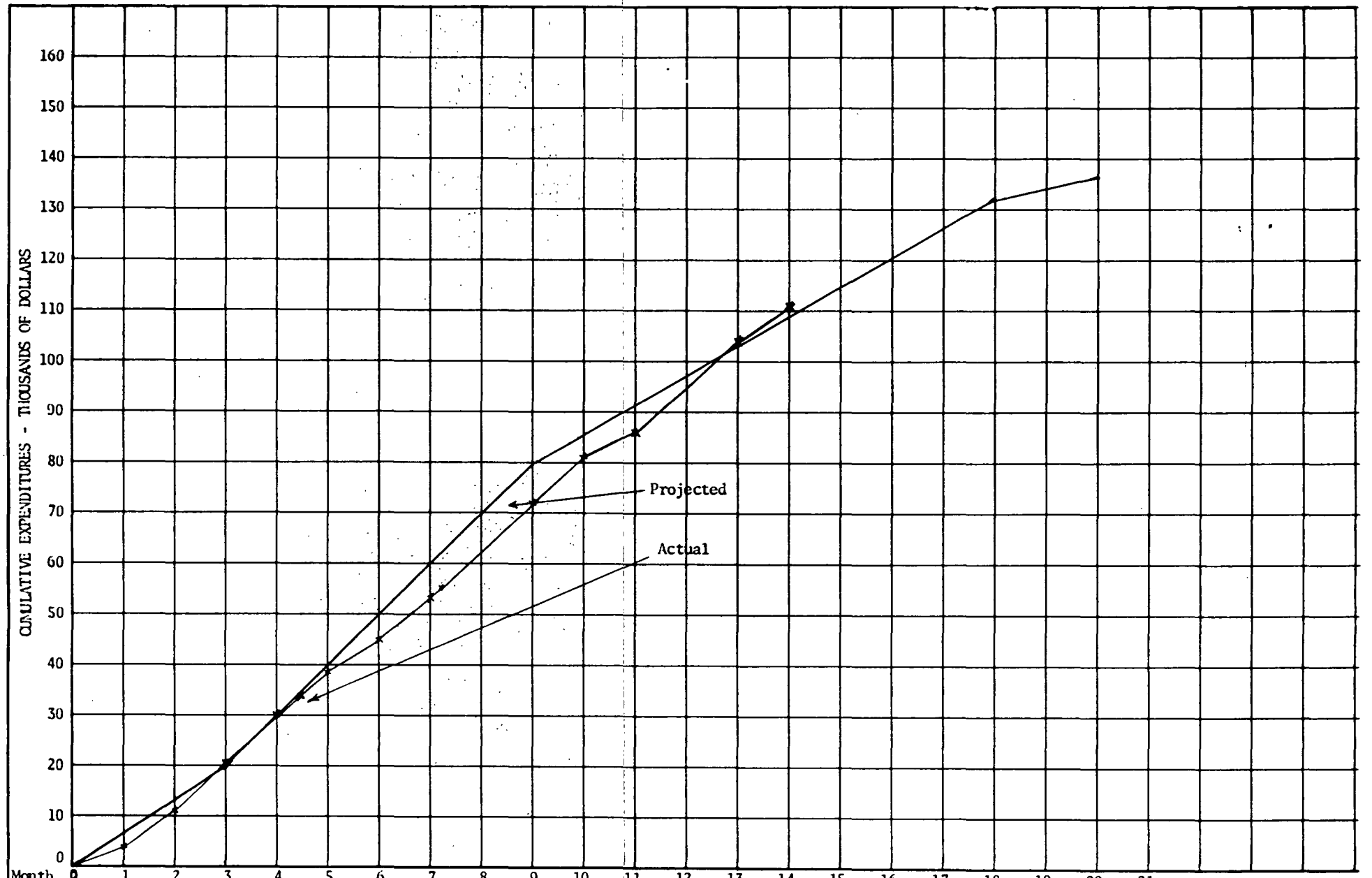
Smelt-Composition	25% Na_2S	25% Na_2S	25% Na_2S
	75% Na_2CO_3	70% Na_2CO_3	75% Na_2CO_3
	0.01% Na_2SO_4	2.79% Na_2SO_4	Graphite Crucible
Conversion Factor	1.5	0.33	>>25

TABLE II

PREDICTED VS ACTUAL EFFECT OF Na_2SO_4

ON CONVERSION FACTOR $\frac{P_{H_2}}{P_{H_2O}}$ (1600°F)

Ratio $\frac{\left(\frac{P_{H_2}}{P_{H_2O}}\right)_{.01\ Na_2SO_4}}{\left(\frac{P_{H_2}}{P_{H_2O}}\right)_{2.79\ Na_2SO_4}}$	Predicted	Actual
	4.2	4.5



SUBJECT ANTICIPATED EXPENDITURE VS TIME CURVE, INVESTIGATION OF SMELT-WATER REACTIONS FOR FOURDRINIER KRAFT INSTITUTE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

AL. 74

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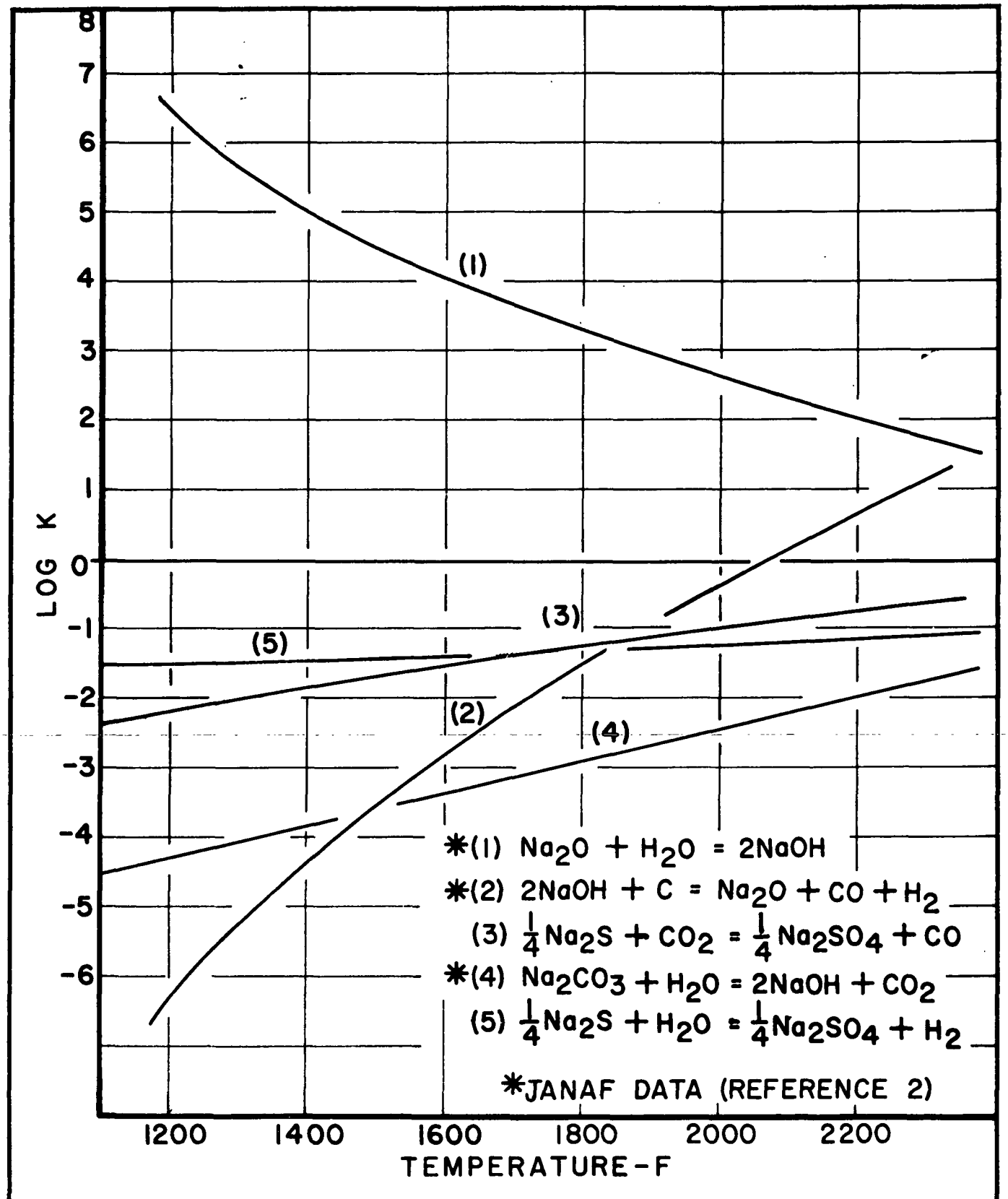


SUBJECT: EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	DRAWING NO. KB

FIGURE 1

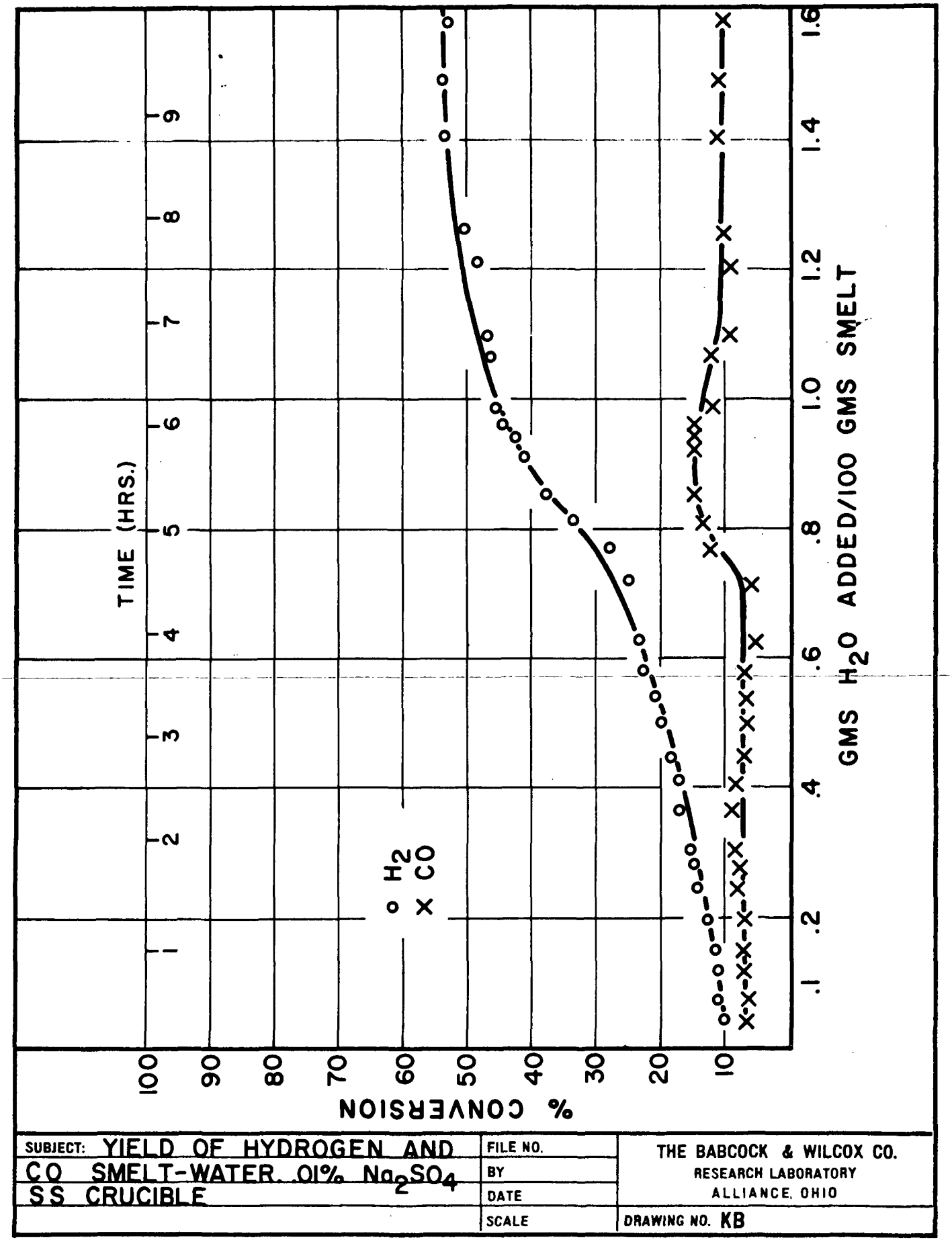
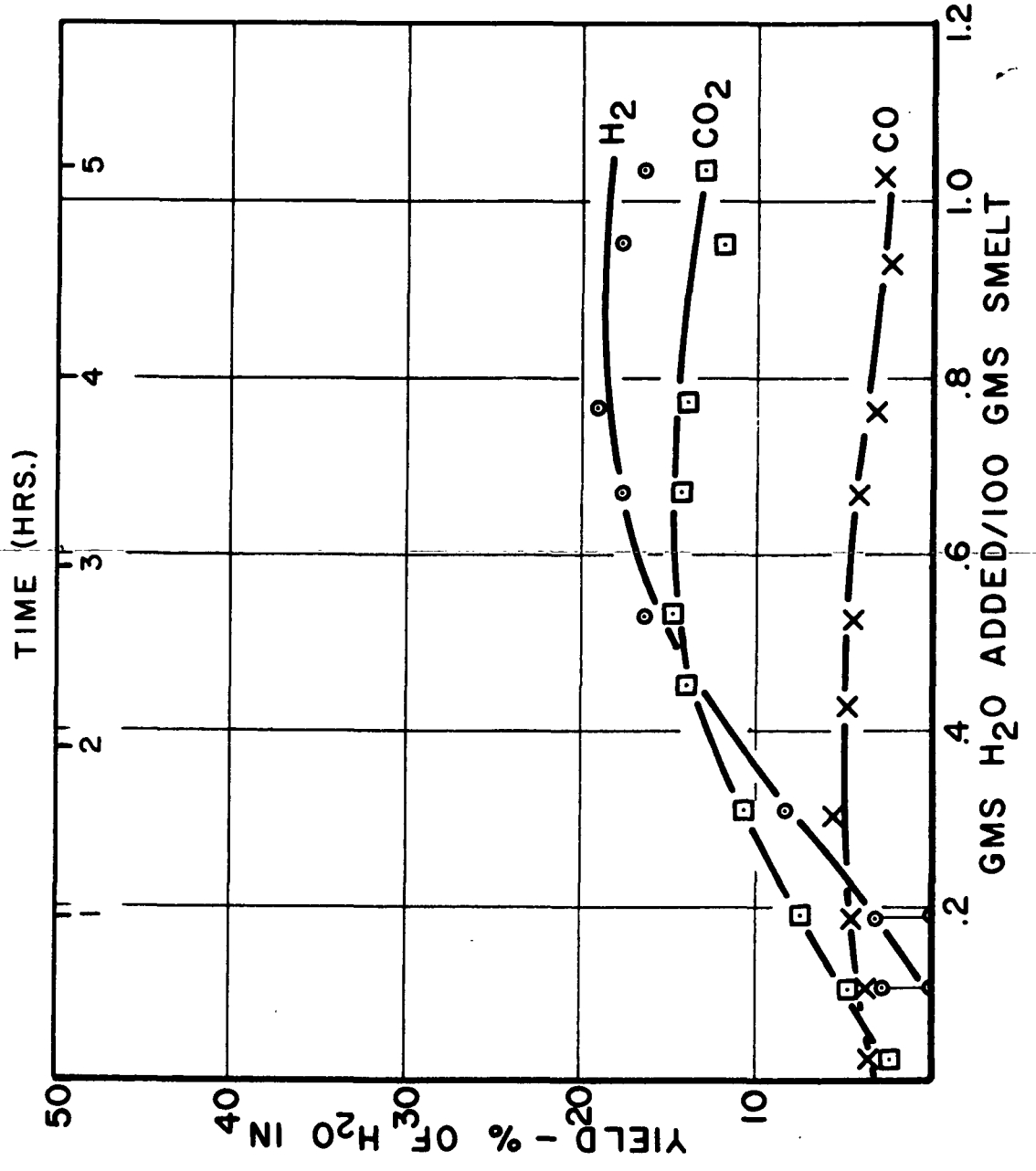

TIME (HRS.)
GMS H_2O ADDED/100 GMS SMELT
% CONVERSION
o H_2
x CO
SUBJECT: YIELD OF HYDROGEN AND CO SMELT-WATER. 01% Na_2SO_4 SS CRUCIBLE
FILE NO.
BY
DATE
SCALE
THE BABCOCK & WILCOX CO.
RESEARCH LABORATORY
ALLIANCE, OHIO
DRAWING NO. KB

FIGURE 5



SUBJECT: YIELD OF H_2, CO, CO_2 FROM	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
WATER-SMELT REACTION - 2.79%	DATE	
Na_2SO_4	REV.	DRAWING NO. KB

FIGURE 7

TRIMONTHLY PROGRESS REPORT
COVERING WORK FROM MARCH 6, 1965 THROUGH JUNE 5, 1965

to

Dr. H. S. Gardner, Project Coordinator
The Institute of Paper Chemistry

Submitted by
Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

NO. 5 PROGRESS REPORT ON THE COMBUSTION ENGINEERING PROGRAM FOR DETERMINING THE NATURE OF AND REMEDIES FOR EXPLOSIVE REACTION(S) BETWEEN SMELT AND WATER IN KRAFT CHEMICAL RECOVERY FURNACES

I. Explosion Mechanism

1) Similarity to Hot Metal Quenching

An interesting parallel between the effect of variables on smelt-water explosions and on quenching hot metal specimens has been uncovered in several literature references reviewed recently. The data of Pilling and Lynch[1] on quenching hot metal cylinders in water have been reproduced in Figure 1. This figure shows a characteristic cooling curve for the center of a small (6.4 mm) cylinder of steel heated to an initial temperature of 1526°F and plunged into tap water at 158°F. Cooling in period A by conduction and radiation is slow due to the presence of an insulating vapor blanket which greatly retards heat transfer and also to the time lag for conduction of heat from the center to the surface. The survival of this steam jacket depends on the relative rates at which heat is delivered through the jacket to the boundary surface between steam and water, and is removed from it by the adjacent cooler layers of water.

As the steam envelope disappears, periodic liquid contact between the hot surface (still far above the boiling point) and water is initiated during period B. Vigorous boiling ensues and each minute bubble of steam formed is whirled away by the forceful local convection currents and immediately condensed. This is the vapor transport phase of cooling during which metal temperature is reduced rapidly.

In the third stage, C, the metal surface is cold enough so that no vaporization occurs; hence heat is lost from the metal by liquid conduction and convection. This stage, like the first, is characterized by slow cooling.

French[2] showed that small differences in the temperature of water used for quenching had a pronounced effect on the rate of cooling of 0.5" diameter steel cylinders. Some of these data are reproduced as Figure 2. Water temperatures in the range 176° to 211°F slowed cooling significantly. The decrease in rate is due to an extension of phase A cooling by elevation of vapor pressure of the water. This prolongs the life of the vapor blanket.

Further data from French[2] in Figure 3 show that thermally stable dissolved electrolytes like sodium hydroxide greatly

increase cooling rate (heat transfer rate). Such materials decrease the life of the vapor envelope surrounding the hot metal cylinder and hence greatly shorten period A of vapor-blanket cooling.

Still further data from French[2] in Figure 4 show the effects of dissolved gases in quench water on surface cooling rates of 1" diameter steel spheres. The nature of the dissolved gases can cause widely different results. In both cases illustrated, the gas was passed through the water for a considerable period to produce saturation at atmospheric temperature and pressure before quenching. The fact that carbon dioxide was more effective in retarding the cooling may be ascribed in large part to its high solubility in water. Scott[3] mentioned that soap solution likewise greatly increased the duration of vapor phase cooling.

The influence of these variables on quenching rate of hot metal specimens qualitatively parallels our experience with water injections into hot smelt if one keeps in mind the tenet that smelt-water explosions are dependent on the rapid transfer of heat from smelt to water. For instance:

1. Smelt has an upper explosive temperature limit of about 1700°F. Hotter smelt would be expected to prolong the life of a vapor envelope and hence phase A cooling.

2. Water above 187°F consistently did not explode on injection into molten smelt. Again, the tendency to vapor blanket at elevated coolant temperatures parallels metal quenching behavior.

3. Thermally stable salts like NaOH, NaCl, Na_2SO_4, and smelt dissolved in the water injected into molten smelt greatly increased explosive violence. This is presumably because their presence decreased vapor film life as with metal quenching and shortened the inefficient heat transfer period A.

4. Ammonium bicarbonate, methyl alcohol, and ammonia solutions in water prevented smelt explosions and would (like the dissolved CO_2 in Figure 4) tend to impede heat transfer.

5. Wetting agents in injected water retarded explosions just like soap dissolved in quench water retarded cooling of hot metal specimens.

(2) Heat Transfer Calculations

A computer calculation study of heat transfer rates for encapsulated water was conceived and executed by Mr. B. Teigen

of KDL, Combustion Engineering, Inc. His findings from this detailed program are summarized in the accompanying report. He reached three main conclusions from the study:

1. The concept of water encapsulation by molten smelt violates no basic principles of physics or heat transfer.

2. The contents of a capsule at time of rupture must be principally hot water rather than steam as origirally postulated. Pressure increase before rupture must be due largely to volumetric expansion of the water, rather than to creation of steam.

3. A vapor (steam or other gas) film between the smelt shell and liquid water inside the capsule is of primary importance in limiting heat transfer rate and hence shell thickness. Even a 0.0003" thick film would significantly slow heat transfer and reduce capsule thickness by half. This film would also reduce pressure buildup since water could expand into the compressible space occupied by the vapor film.

These conclusions allow a mathematical explanation for the beneficial effects of vapor film promoters in both hot metal and molten smelt quenching experiments. They also necessitate a slight revision in the encapsulation theory. Since capsule rupture occurs before steam is generated in the capsule, this rupture must be the triggering explosion mentioned by Long[4] which causes intimate mixing of atomized particles of hot water traveling at high velocity through the surrounding body of molten smelt. The high velocity of these particles and their large area of surface contact with smelt would greatly increase the rate of steam generation. Thus, an encapsulation explosion is probably due to explosive generation of steam initiated by capsule rupture. If heated to 1500°F by such contact, each volume of water could form 4960 volumes of steam (1700 volumes if not superheated), thus the process fulfills the original definition of an explosion.

Mr. J. E. Hay, Research Physicist at the Bureau of Mines Explosive Research Center, has suggested by letter of February 8, 1965 that a single 3 ml. injection of water may form a cluster of small capsules rather than one large one. If the pressure in several reached a point near their bursting strength, the explosion of one would send out a shock wave which would trigger the explosion of others. He remarked that:

"The energy released by the latter would in some degree support the shock against the decay in amplitude expected of a wave originating from a point source; thus, the shock would proceed detonation-like through the cluster."

A small diameter for an individual shell would require less tensile strength for containment of a given pressure. However, for a smaller capsule, the pressure would become much greater due to the more rapid heat transfer rate. Thus, in a dynamic system the tensile strength advantage gained by a smaller diameter might be overcome by the greater pressure increase which developed.

3) Inert Atmosphere Experiments

(a) Introduction

An explosion was defined in earlier reports as a very sudden release of gases at high pressure. No explosive (exothermic) chemical reaction which generates combustible gases (like H_2, CO, CH_4) has yet been identified by the thorough studies in progress more than a year. None has been identified which produces free oxygen. Therefore, any explosive chemical reaction due to smelt-water contact must be a combustion of flammable gas in the oxygen supplied by air. If the smelt-water explosions in chemical recovery boilers are combustible in nature, inerting the furnace should be an adequate preventive measure. If an explosion does occur in an inert atmosphere, it must be due to one of two causes: (1) an as-yet still unidentified non-combustible type highly exothermic chemical reaction or (2) a physical smelt-water reaction.

Smelt dissolving tank explosions had been shown by previous work to take place on the bottom of the tank far beneath the surface of the green liquor. Here air (gaseous oxygen) would be almost totally absent, and so a combustible type explosion could not occur. The present type of explosion with inverted smelt to water ratios, however, made it desirable to check earlier conclusions using this modified ratio.

(b) Equipment

The spherical explosion vessel shown in Figure 5 was designed and built so that composition of the atmosphere surrounding smelt in contact with water could be controlled. Products of the explosive reaction, both gases and solids, can be recovered for analysis. This vessel has the additional advantage of ability to contain safely explosions of a much higher order of violence than possible with the 3/4" thick plywood barrier used first. Remedial measures can likewise be tried on an increased scale. This figure shows Mr. Charles Norton bleeding gas samples from the sphere into gas pipettes for analysis by gas chromatography. A vacuum pump for air removal is shown on the right. The horizontal rod in the foreground contains a high pressure piezoelectric quartz transducer for measuring pressure waves produced by smelt-water explosions.

The vessel weighs approx. 2500 lbs. and is 47" I.D. It is made of 1.25" thick SA212-B steel and designed to withstand 500 psi at 600°F. The volume of the sphere, including six flanges, is 31.6 ft.^{3}.

Figure 6 is a diagram showing component parts of the spherical explosion vessel. A is a high-pressure sight glass. B is a quick closure lid seated with "O" ring. C is a 100 watt light. D is the 1/8" I.D. water injector line and E, the N_2 flushing line. F is a thermocouple mounted to ride up and down on piston N. The thermocouple is connected by lead wire H with a Speedomax H recorder outside the sphere. G is the graphite crucible containing approximately 500 grams (slightly more than a pound) of molten smelt in the temperature range 1500-1700°F at the time of injection. I is the shaft of the pressure transducer probe. The sensing head is of course in the end nearest the crucible. Electrical connection from the transducer is made outside the sphere to a charge amplifier, a power amplifier, and a Visicorder which records the pressure wave. J is the supporting floor structure. The lower flange of the sphere and pneumatic piston mechanism K extend into an already constructed pit. L is a 16" manhole with Flexatallic gaskets and hinged inward-opening door.

Figure 7 shows instrumentation of the sphere grouped nearby. From left to right these instruments are as follows: Speedomax H temperature recorder, Visicorder, power amplifier, charge amplifier, DC power supply (for the timer above), and automatic water injector (with N_2 pressure supply cylinder).

(c) Procedure

A 500 gram charge of smelt, made up of high assay dried fused commercial grade sodium sulfide and C.P. anhydrous sodium carbonate to contain 30% Na_2S was placed in a covered graphite crucible in a stainless steel cup with "ears" for safe handling. Graphite was chosen after a number of other materials including stainless steel and zirconia had proved too corrosion-prone to be useful. Air in the test sphere was rapidly removed with the large vacuum pump and the vessel quickly filled with commercial grade oil-pumped nitrogen containing 0.06% oxygen. It was then pumped down again and refilled with nitrogen. The same procedure was repeated a third time. The nitrogen flow was adjusted to approximately 5 psi positive pressure in order to minimize inleakage of air. A sample of gas was taken from the sphere after approximately 20 minutes for analyses on the gas chromatograph to assure oxygen level below any

flammable limit. Next the smelt charge was melted rapidly in the high frequency induction furnace shown in Figure 8 and maintained at approximately 1800°F prior to manual transfer to the test sphere. Piston N was raised by pneumatic cylinder K up into port B and the quick closing lid opened. At this time approximately a 1/8" clearance existed between the piston and the port walls. The positive flow of nitrogen around the piston, however, prevented appreciable air inleakage while loading the hot crucible of smelt on the piston.

Next, the smelt crucible was sampled and transferred to the piston. The thermocouple F was inserted into the smelt. The piston was lowered just enough to clear the top of the thermocouple and the quick-closing lid B closed and bolted in place. Nitrogen flow was cut off. Then the piston was retracted full distance so that the smelt surface was at approximately the center of the sphere. An additional gas sample was taken to check air inleakage while smelt cooled to the proper range. Water injection tube D was then thrust over the crucible and the water injection button pressed to inject forcibly 3 ml. portions of room temperature water (or 10% smelt solution in water) first to waste, in order to clear the line of hot liquid, and then beneath the surface of the molten smelt from a nozzle 2" above. Explosion wave pressures were registered on the Visicorder.

A snubbed gage on the outside of the sphere was used to measure volumetric pressure buildup in the sphere. Generally 3-5 psi resulted. Explosions were observed through the sight glass both in the darkness and with the light on. Samples of gas were collected at several time intervals in order to insure adequate mixing in the sphere. Gases were also smelled to test qualitatively for H_2S. Finally pressure was relieved and the sphere opened. Smelt was removed from key locations in the sphere and the samples stored under nitrogen in a desiccator prior to analysis.

(d) Results

An explosion equivalent in every way (except noise) to those in air was produced in each of the four tests in this inert atmosphere. Explosions were observed through the high-pressure sight glass. One run (#4) was observed with the light off. Neither of two observers saw any light created by the explosion. Smelt was blown from the crucible and plastered in paper-thin sheets over the top half of the sphere. The 1/2" thick graphite crucible was shattered in three of the four experiments. Smelling the exit gas bled from the sphere following an explosion gave a slightly "burnt" odor, but no hydrogen sulfide. Gas chromatographic analysis later showed no hydrogen sulfide or "strangers", ie, unidentified peaks on the chromatograms.

There was no typical explosion noise outside the sphere. A sharp "ping" as if the sphere had been struck a stout blow with a ball pein hammer was the only noise produced by explosions. (The

Bureau of Mines had reported that TNT also produces this type of noise when detonated in a sphere.) Visicorder traces of wave height and velocity were typical of explosions produced in air in the plywood explosion barrier. Visicorder traces showed peak pressures of 90.1 psi 1.75" away from the crucible top and a duration of about 0.003 second. It should be kept in mind that (a) pressure waves decay rapidly with distance and that (b) this pressure represents a substantial concentration of energy release from such a small volume (3 ml.) of water injected into smelt and (c) the peak localized pressure quoted is far above the level which furnaces are built to withstand.

A U.S. Bureau of Mines publication[5] states that "no mixture of hydrogen, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 4.9% oxygen." Figure 9 reproduced from this reference shows that combustible gas mixtures could not have existed in the sphere with the very small proportions of oxygen present (0.31-0.76%) at the time of explosion. (See Table 1) The deviation of these test conditions from atmospheric would not, according to other data in the bulletin, have allowed the gas mixtures to become explosive.

These initial tests were designed to evaluate effect of inert atmosphere and not for quantitative analyses of the resulting products. Relatively small quantities of reactants (in relation to sphere volume) were employed. For instance, if the 3 ml. of water had been converted quantitatively by chemical reaction into hydrogen, the resulting concentration of hydrogen would have been only 0.4% by volume. Analyses of smelt samples before and after explosions were run. These are recorded in Table 2. Sulfate seems to have decreased while sulfide increased. This may have been due to reaction between sulfate and graphite crucible while the smelt was cooling. The data do not show a clear trend about the effect of explosions on smelt composition.

4) Explosion Pictures

Photographing smelt-water explosions has proved unusually difficult due to: (a) their non-luminous character (b) the opacity of the smelt and (c) the high temperature and corrosive, equipment-damaging nature of the smelt itself. Six lighting set-ups, one with a 3' diameter rented D-C powered carbon arc searchlight, were tried before satisfactory pictures were produced. More than forty 400' rolls of color film have been taken. A rented model K1004 Hycam motion picture camera and high speed Ektachrome ERB (ASA-250) film were employed in all photographic studies. The methods used for filming were discussed in C.E. No. 4 Progress Report. No variation of smelt composition was found which increased the transparency of smelt enough to actually see through appreciable thickness of it.

The best lighting technique devised by Mr. Tung Nathan and Mr. Douglas Wayne of K.D.L.'s photographic laboratory to date has

been to apply high light intensity as close to the explosions as possible, as shown in Figure 10. The smelt crucible was placed in the center of a "C" shaped bracket containing three 750W G.E. Photofloods (#750R). A Follow Spot and a High Spot 1000W quartz-iodine light (both produced by the Color Tran Co.) were suspended at either side about two feet above the crucible. Pictures were taken in the plywood booth rather than in the sphere to allow ample room for the bulky lighting equipment involved. A new 45° angle safety glass window allowed placement of the camera itself much closer to the explosion.

Figure 11 is a black and white print of typical 16 mm color pictures taken with this technique. This particular series of seven pictures was taken at 4500 frames per second. Although not apparent from the print, the explosive burst was non-luminous. The white color appeared to be due to light reflected from a cloud of steam. Some idea of the volocity of the explosion can be gained from comparing frames #0 and #0+1. Here the explosive burst increased in volume by 400% in 1/4500 of a second. Bubbles did not seem to issue from smelt surface in the approx. 0.030 second delay between injection and explosion. We feel that high speed photography has added much to a better understanding of explosion mechanism.

I. Smelt Additives

Twenty additional quenches have been made of smelt containing various additives in an attempt to find one which inhibits smelt-water explosions over a normal range of smelt compositions. These make a total of 118 experiments on this approach alone. Ten percent $CaCO_3$ retarded violence in a number of cases, but its effect was not consistent, especially with smelt above 25% Na_2S. A definite correlation, noted in the first progress report by Dr. A. L. Plumley, between Na_2S content of the smelt and its tendency to explode has been observed. If smelt has less than about 20% Na_2S it is difficult to explode with water (but not green liquor) injections. An increase to 24% Na_2S makes smelt explode readily. Higher Na_2S than this makes it even more explosive. As in the case of dissolving tank explosion experiments, the addition of small proportions of sodium chloride or sodium hydroxide to smelt at the 20% Na_2S level caused it to explode on contact (injection) with water. A number of tests were run using this lower sulfide "sensitized" smelt to screen various smelt and quenching solutions.

III. Smelt Quenching Solutions

The explosion-preventing effect of high vapor pressure additives in water used for quenching kraft smelt was discussed on pp C-4 and C-5 of the CE No. 3 Progress Report covering the

period August 15 to November 6, 1964. Explosions were entirely eliminated by including 10% by volume of methyl alcohol, 10% by weight ammonium bicarbonate, or 5% by weight ammonium hydroxide in the water injected into molten smelt. A later report showed that even hot water alone, if above 187°F, prevented explosions. The beneficial effect of the hot water was nullified, however, when it contained 10% of dissolved smelt.

All of these explosion-inhibiting aqueous solutions have one important common characteristic, a vapor pressure considerably above that of cold water when injected into smelt. Mr. Teigen's heat transfer calculations confirm the significance of even a thin vapor barrier around a submerged globule of water in retarding the rapid heat transfer from smelt to water which we believe is necessary to initiate a physical smelt-water explosion. The chief disadvantage of previously reported ammonium bicarbonate and ammonia solutions as explosion inhibitors lies in their lack of thermal stability when stored under plant conditions. Alcohol solutions would of course be impractical since they present a flammable hazard in a furnace.

The continued search for other quenching solutions which avoid this drawback has turned up one very interesting candidate, ammonium sulfate. This material is thermally stable to about 540°F and does not decompose in solution at the boiling point of water. It has proven highly effective for preventing smelt-water explosions over a wide range of concentrations, smelt sulfidities, and quenching conditions as shown by data in Table 3. Its beneficial action is probably based on the following chemical reaction between ammonium sulfate and alkaline smelt, rather than thermal decomposition, to yield the desired vapor blanket.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2\ H_2O$$

The sodium hydroxide would come from hydrolysis of sodium sulfide and carbonate in solution.

Runs 1 and 2 were blanks to establish the explosiveness of 20% Na_2S smelt sensitized with 5% NaCl upon water injection. The 20% Na_2S smelt without NaCl did not explode with either method of water addition. Runs 3-5 showed that 10% $(NH_4)_2\ SO_4$ solution prevented explosions when injected or added in a steady stream (simulated tube leak method of addition) at 80 ml. per minute on the smelt. In Runs 6 and 7 the 10% $(NH_4)_2SO_4$ solution was effective on even the more explosive high sulfide smelt. Runs 8 and 9 showed that 5% may be a lower practical limit of concentration for inhibition of explosions. Runs 10-12 showed that low-sulfide, NaCl-sensitized smelt can be quenched with a minimum 2% solution. Forty percent solution, which is near the solubility limit of ammonium sulfate, was also effective in Run 12. Runs 13-15 indicated a slight extension of inhibition by inclusion of a 0.01% solution of FC-170 surface active agent. A repeat with 5% solution in Run 18 (compared to Run 16) suggested some benefit of the surfactant here also.

The next experiments were run with a "safe" 10% level of $(NH_4)_2SO_4$ on high sodium sulfide smelt. The conditions of quench were varied to approximate some which would occur in a plant. The very high Na_2S level smelt in Run 19 did not cause an explosion with tube leak addition of 10% solution; neither did it explode when the solution was added hot (200°F) in Run 20. A 2" black ash layer on smelt in Runs 21 and 22 did not prevent inhibition of explosions. Cold 40°F solution in Run 23 seemed to be just as effective. A 1/2" thick layer of 65% black liquor on the surface of the smelt in Run 24 did not impair the effectiveness of forcibly injected solution.

Runs 25 - 28 were made to compare the effectiveness of $(NH_4)_2SO_4$ solution on samples of plant smelt from two mills with its effect on the synthetic smelts used to date. The violent explosion of plant smelt in Run 25 with 16.4% Na_2S indicated that this sample contained sensitizers which made it more explosive than a synthetic smelt of the same Na_2S content. Explosion was prevented entirely in Run 26 by injection of $(NH_4)_2SO_4$ solution. The effectiveness of this quenching solution was again demonstrated in Runs 27 and 28 with smelt from a different mill. A tube leak addition of concentrated 30% solution prevented explosions in Run 29 as did also the concurrent tube leak at equal rates of both 30% $(NH_4)_2SO_4$ solution and water in Run 30.

The fact that $(NH_4)_2SO_4$ is an effective inhibitor over the range 5% to 40% implies that an eight-fold dilution by tube leak would be possible before loss of inhibiting effect. This salt is attractive also in that its decomposition and reaction products would not contaminate the recovery system. It is cheap, non-toxic, readily-available and used generally as a fertilizer component and in fireproofing fabrics. The results to date are very encouraging and indicate that there is a good possibility of developing a safe, rapid emergency shutdown procedure based on application of aqueous quenching solutions to the hot ash and molten smelt in a kraft chemical recovery furnace.

IV. Black Liquor Applied to Smelt

While water-free black liquor solids are a fuel*, the concentrated black liquor supplied to furnace guns is not. The normal 30% of water in concentrated liquor delivered to the furnace effectively prevents its combustion. The first step in burning black liquor is a final drying operation in the hot furnace atmosphere; either flash drying in suspension by one system of operation or wall drying in the other. One means of extinguishing the fire in a burning bed is to cover it with cool or poorly atomized black liquor. Black liquor as a fuel has another unusual property. This is the tendency to form a layer of char on application directly to the bed or to smelt which may impede contact of molten smelt below with water from a tube leak.

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*Black liquor as fired to the furnace has roughly about one-third the heating value of coal.

It was decided by Mr. Charles Norton and the writer to explore this possibility by a series of simple laboratory tests. A number of 500 g batches of smelt of 29 to 33% Na_2S content were melted and 180°F 65% solids kraft black liquor was applied to the surface of the smelt at 1600-1800°F allowing varying periods of pyrolysis from 30 seconds to 2 minutes. A few lazy flames of burning pyrolysis gases appeared after about 20 seconds and disappeared after another 10 seconds. A series of water injections on the top of the char were then made. Those crucibles to which only 50 g of black liquor was applied exploded violently on subsequent multiple 3 ml. injections of water. However, when 150 to 250 g of black liquor was poured on the surface of the smelt, a 2" depth of char was generated. Repeated injections of water on this char layer no matter how forceful, or tube leak additions of water, did not produce an explosion in eight duplicate experiments. Evidently the char created had effectively sealed the surface of the molten smelt against water penetration.

We believe this experience demonstrates a desirable aspect of black liquor quenching not considered previously. Of course a water leak might tend to wash away black liquor before it had carbonized sufficiently to develop a protective water-insoluble layer of char. Dilute black liquor below 35% solids can cause a smelt-water explosion. But on the other hand, as is developed further under Discussion, bed washing action from a small leak may be delayed until the boiler has lost considerable pressure. This delay might allow a sufficient period for development of a sealing char layer.

Further laboratory work would of course be required to define the limits of this approach. To date, however, it seems that the copious application of concentrated black liquor to smelt would be a better preventive measure for smelt-water explosions than a shallow layer. A small spraying of liquor on the bed would give an inadequate protective char layer and a higher proportion of flammable pyrolysis gases to inerting steam (from the 30% water content) than a deep layer of black liquor.

V. Discussion

One way to take a furnace off line more safely once a leak of uncontrolled water into the furnace cavity has been discovered may be to cool all of the smelt in the furnace rapidly below the 1500-1700°F range in which it explodes on contact with water. Maintaining the smelt above 1700°F by applying auxiliary fuel guns near the bed does not seem as attractive because of (a) the difficulty in supplying heat fast enough to the limited area where water from a tube leak strikes due to the very rapid removal of heat, as heat of vaporization, by the steam generated and (b) the increased chance of an auxiliary fuel explosion if a smelt-water explosion did occur.

In many cases the substantial delay between tube leak discovery and resulting explosion might allow time for smelt cooling, if this could be done quickly and safely. Previous reports have indicated that this delay may be due to (a) the time necessary to cool smelt down to the explosive range and place liquid water beneath smelt surface and (b) the time for water from a tube leak to dissolve smelt (i.e., form green liquor on the bed) and thereby become much more explosive with smelt.

Mr. R. C. Patterson and Mr. F. W. Hochmuth have pointed out that the type of leak itself could greatly influence this time delay. For instance a small leak in a pressure part would be expected to spray boiler water over a considerable area of smelt bed due to a sizeable portion of it flashing into steam at the fissure. Such spray (unless it hit a furnace wall) would (a) permit relatively little penetration of liquid water below the smelt surface and (b) promote evaporation as fast as the water was added to the large area of smelt bed. A large tube split, however, could cause rapid decay of pressure in the entire boiler which would soon eliminate flashing and atomization. In this case, and also with a leak from a non-pressurized water cooling coil, a substantial unshattered stream of liquid water might strike the bed and greatly increase the chance of a smelt-water explosion after only brief delay.

The laboratory testing of ammonium sulfate and other additions to accessory quenching water is continuing. Additions to boiler water itself, while theoretically more attractive, are not practical. Boiler water must maintain very low solids content to prevent scale, corrosion, and carryover. Rather sizeable proportions of chemicals in water (by boiler water purity standards) are required to inhibit explosions. In addition, none of the effective additives to date would be stable in hot, alkaline boiler water.

The guiding thought behind tests on aqueous solutions is that water has an excellent ability to quench hot material quickly due to its large specific heat and heat of vaporization. (Even considering vapor blanket formation, water has 25 times the quenching ability of air on hot metal[6]). If additions to quench water could be found which would render it non explosive with smelt, possibly the smelt could be sprayed with the solution and cooled in the grace period before a leak of boiler water caused an explosion. Vaporization of aqueous quench solutions would produce approximately a 1700 fold volume increase of steam. If the steam were in sufficient volume, it would also serve to inert quickly any flammable gas mixture in the furnace cavity against a combustible explosion. Various systems for application of a quenching spray can be envisioned. One might be an emergency button which when pressed after a tube leak had been discovered, would cut off the black liquor supplied to the guns and substitute aqueous quench solution. Solution would be distributed over the bed by the oscillating motion of the guns.

VI. Conclusions

Experimental results in the current report prove that smelt-water explosions of the type studied in this laboratory can take place in an inert gaseous atmosphere. Consequently these results cast serious doubt on the value of furnace inerting or dilution of furnace gases with excess air as a preventive measure for physical smelt-water explosions. The analogy between the effect of a number of variables on hot metal quench rate and on physical smelt-water explosions is surprisingly close. This together with inert atmosphere explosions, and computer calculations of factors affecting heat transfer between water and smelt in Mr. B. Teigen's accompanying report lend additional credence to a physical smelt-water explosion mechanism. While no feasible smelt additives have been found, considerable progress has been made in devising an aqueous smelt quenching solution to be applied in the furnace once a water leak has been discovered.

VII. Future Work

With approximately 6 months of contractual study remaining, it seems apropos to compare briefly C.E.'s March 2, 1964 outline of proposed study with the program covered to date. We believe that most of the essential phases of investigation proposed, which were slanted strongly toward developing a better knowledge of explosion mechanism, have now been covered. Two phases not originally considered but which have added substantial knowledge of smelt-water explosion phenomena were high speed photography by Messrs. Nathan and Wayne and the computer calculations of heat transfer rates in an encapsulation process by Mr. Teigen. The studies of explosion mechanism are now fairly well complete, which leaves the remaining period essentially free for an intensive study of remedial measures.

Chief among these, of course, is a detailed investigation of ammonium sulfate solutions and other possible smelt quenching agents. Here we need to know more about the composition of pyrolysis and reaction products of this material with hot char and molten smelt, in order to assure that none reaches a flammable range. Additional work on concentrated black liquor blacking out should aid to establish whether it is beneficial following a tube leak.

VIII. Expenditures on the C.E. Smelt-Water Explosion Study

Costs (cumulative) of the Combustion Engineering, Inc. study as of May 31, 1965 are itemized as follows:

Labor	$ 31,350
Overhead	51,732
Materials	38,040
	$121,122

The amount billed to the sponsors as of May 31, 1965 was $94,863.29. The actual and proposed rates of expenditure are compared on the appended graph. The heavy expenses of the project are now passed since all major equipment has been purchased and high speed photography, a sizeable cost item, is essentially complete.

Wharton Nelson

WHARTON NELSON
Senior Project Engineer
June 6, 1965

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(2) H. J. French, "The Quenching of Steels", 1930, The American Society for Steel Treating, Cleveland, Ohio.

(3) Howard Scott, "The Problem of Quenching Medis for the Hardening of Steel," Trans. of the A.S.M. 22, July 1934, pp 577-604.

(4) George Long, "Explosions of Molten Aluminum in Water --Cause and Prevention," Metal Progress, Vol. 75, No. 5, May 1957, pp 107-112.

(5) H. F. Coward and G. W. Jones, "Limits of Flammability of Gases and Vapors", U.S. Bureau of Mines Bulletin 503, 1952, p 20.

(6) "The Metals Handbook", 1948 Edition, The American Society for Metals, Cleveland, Ohio.

TABLE 1

GAS ANALYSES FROM INERT ATMOSPHERE EXPLOSION EXPERIMENTS IN THE SPHERE

		% BY VOLUME**			
RUN	TIME OF SAMPLING	O_2	H_2	CO_2	CO
1	After smelt added	0.31	<0.1	0.03	None
"	After explosion*	0.20	"	"	"
"	Final sample, 10 min.	0.40	"	"	"
2	After smelt added	0.26	"	"	"
"	After explosion, 10 min.	0.29	"	"	"
3	After smelt added	0.76	"	"	"
"	10 min. after explosion*	0.82	"	"	"
"	30 min. after explosion	1.00	"	"	"
4	After smelt added	0.31	"	"	"
"	30 min. after explosion*	0.28	"	"	"
"	60 min. after explosion	0.28	"	"	"

*Crucible shattered

**No H_2S or any unidentified gas was found in any run.

TABLE 2

ANALYSES OF SMELT FROM INERTED SPHERICAL VESSEL EXPLOSIONS

RUN	TIME & LOCATION OF SAMPLE	% * Na_2S	% * Na_2SO_4	REMARKS
1	A-Before explosion	29.7	1.84	Crucible broken.
	B-Floor fragments after expl.	31.1	.42	
	C-Top-of-sphere splatter	30.6	.70	
2	A-Expl. dust - sphere bottom	23.8	.45	Moderate explosion.
	B-Smelt sheets from top	23.3	.36	
	C-Chunks of smelt - bottom	24.0	.43	
3	A-Before explosion	23.4	.71	Crucible shattered.
	B-Globular clusters - bottom	23.7	.48	
	C-Smelt sheets from top	21.7	.50	
4	A-Before explosion	30.6	2.82	Crushed crucible.
	B-Top-of-sphere splatter	32.1	.30	
	C-Smelt sheets from top	31.7	.38	

*Values are an average of duplicates; samples were stored in a nitrogen-filled desiccator prior to analysis.

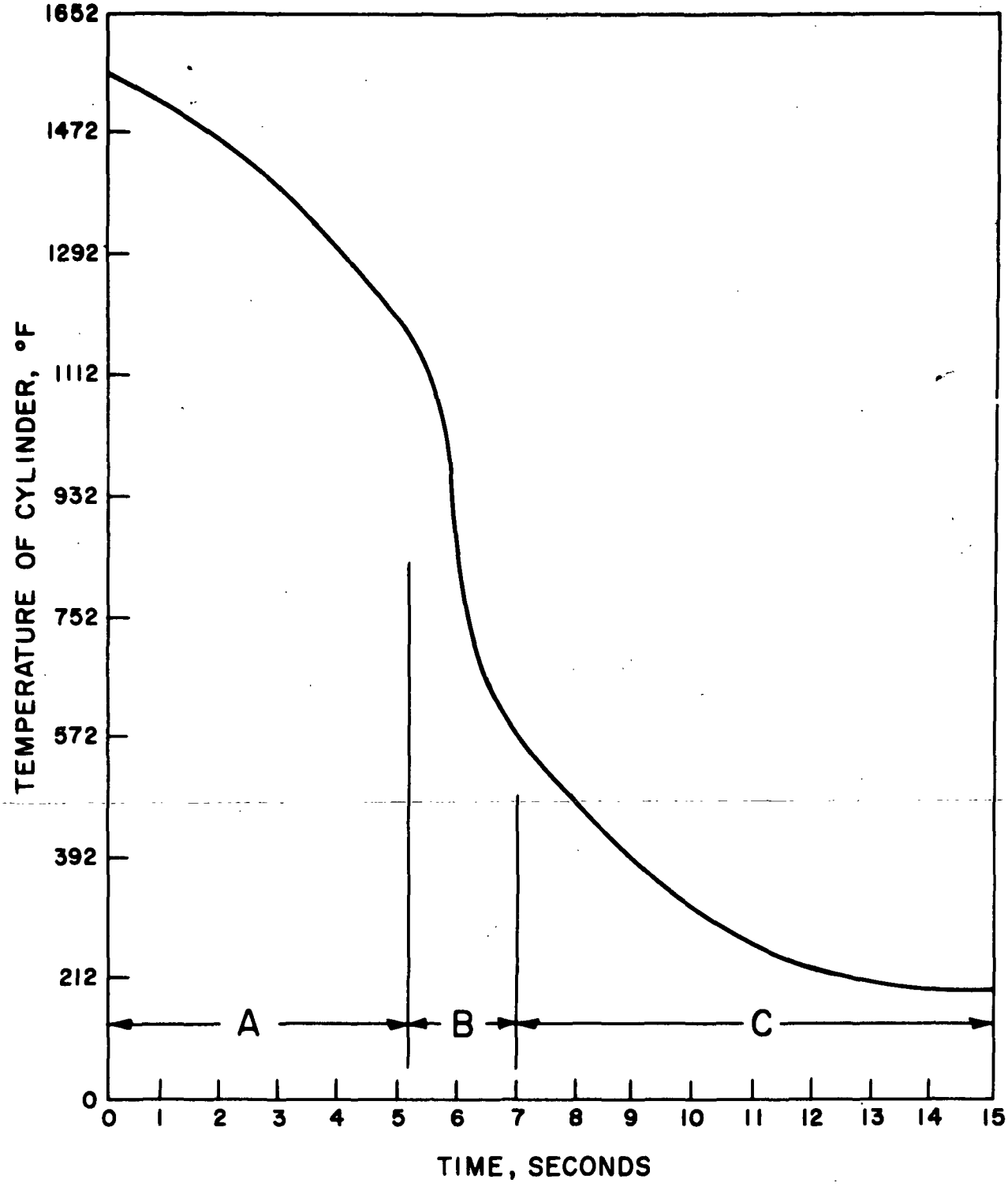
TABLE 3

EFFECT OF AMMONIUM SULFATE QUENCH SOLUTIONS ON PREVENTION OF SMELT-WATER EXPLOSIONS

Run	Smelt Composition* % N_2S	% Other	% $(NH_4)_2SO_4$	Addition	Explosion
1	20.4	5-NaCl	0	3 ml. injection water	Exploded Violently**
2	19.3	5-NaCl	0	Tube leak (simulated) water	Mod. Expl.
3	20	5-NaCl	10	3 ml. injection	None
4	20	5-NaCl	10	3 ml. injection	None
5	20	5-NaCl	10	Tube leak (simulated)	None
6	30		10	3 ml. injection	None
7	25.4		10	Tube leak (simulated)	None
8	25.4		5	3 ml. injection	None
9	26.7		2	3 ml. injection	Exploded**
10	20.2	5-NaCl	2	3 ml. injection	None
11	19.8	5-NaCl	1	3 ml. injection	Exploded
12	18.8	5-NaCl	40	3 ml. injection	None
13	16.0		2	3 ml. injection (soln. with 0.01% FC-170)	None
14	18.7		2	3 ml. injection (soln. with 0.01% FC-170)	None
15	30.3		2	3 ml. injection (soln. with 0.01% FC-170)	Mild
16	29.0		5	3 ml. injection	Surged
17	27.8		10	3 ml. injection	None
18	31.0		5	3 ml. injection (soln. with 0.01% FC-170)	None
19	36.0		10	Tube leak (simulated)	None
20	28.1		10	Tube leak (added hot, 200°F)	None
21	30.0		10	3 ml. injection (2" layer black ash on smelt)	None
22	28.5		10	3 ml. injection (2" layer black ash)	None
23	32.1		10	3 ml. injection (chilled to 40°F)	None
24	30.9		10	3 ml. injection ($\frac{1}{8}$" thick layer of B.L.)	None
25	16.4		0	3 ml. injection(Plant Smelt)	Exploded**
26	16.8		10	3 ml. injection(Plant Smelt)	None
27	23.0		0	3 ml. injection(Plant Smelt)	Mild
28	19.6		10	3 ml. injection(Plant Smelt)	None
29	28.5		30	Tube leak (simulated)	None
30	28.6		30	Tube leak water & $(NH_4)_2SO_4$	None

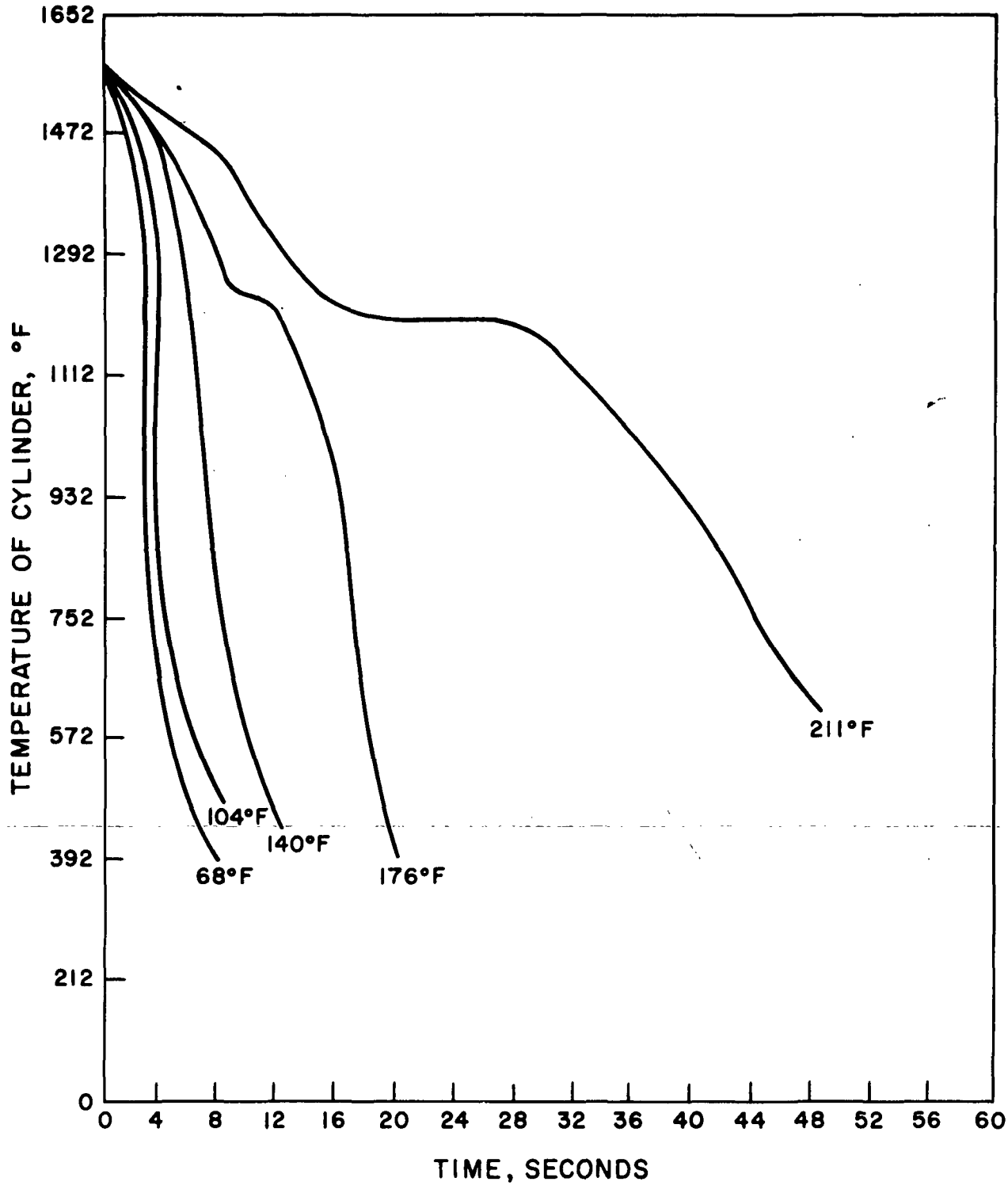
*The balance is Na_2CO_3 in each case.

**Explosion shattered crucible.



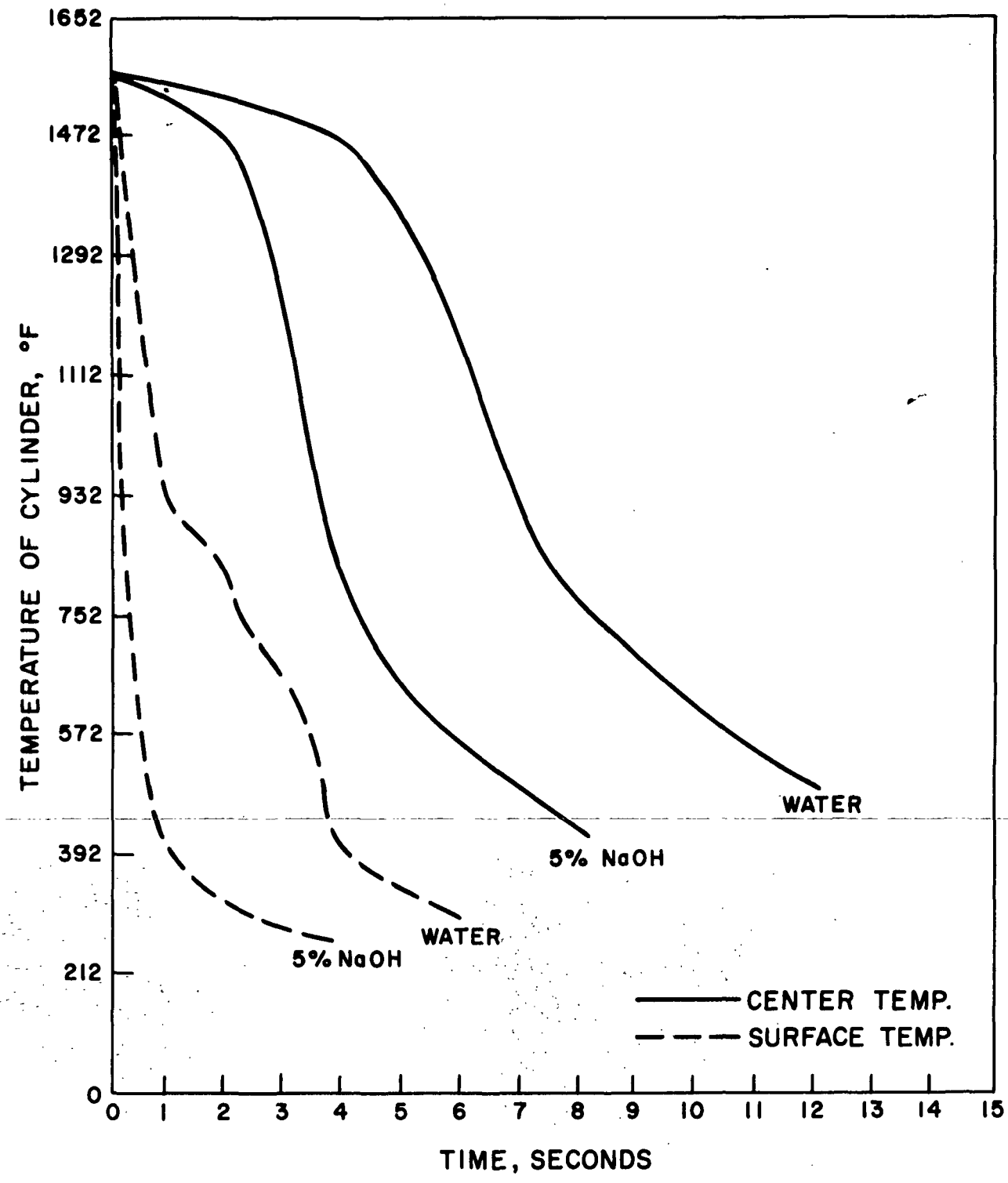
COOLING CURVE FOR CENTER OF A SMALL CYLINDER DURING QUENCHING IN A STILL LIQUID BY PILLING AND LYNCH [1]

FIGURE NO. 1



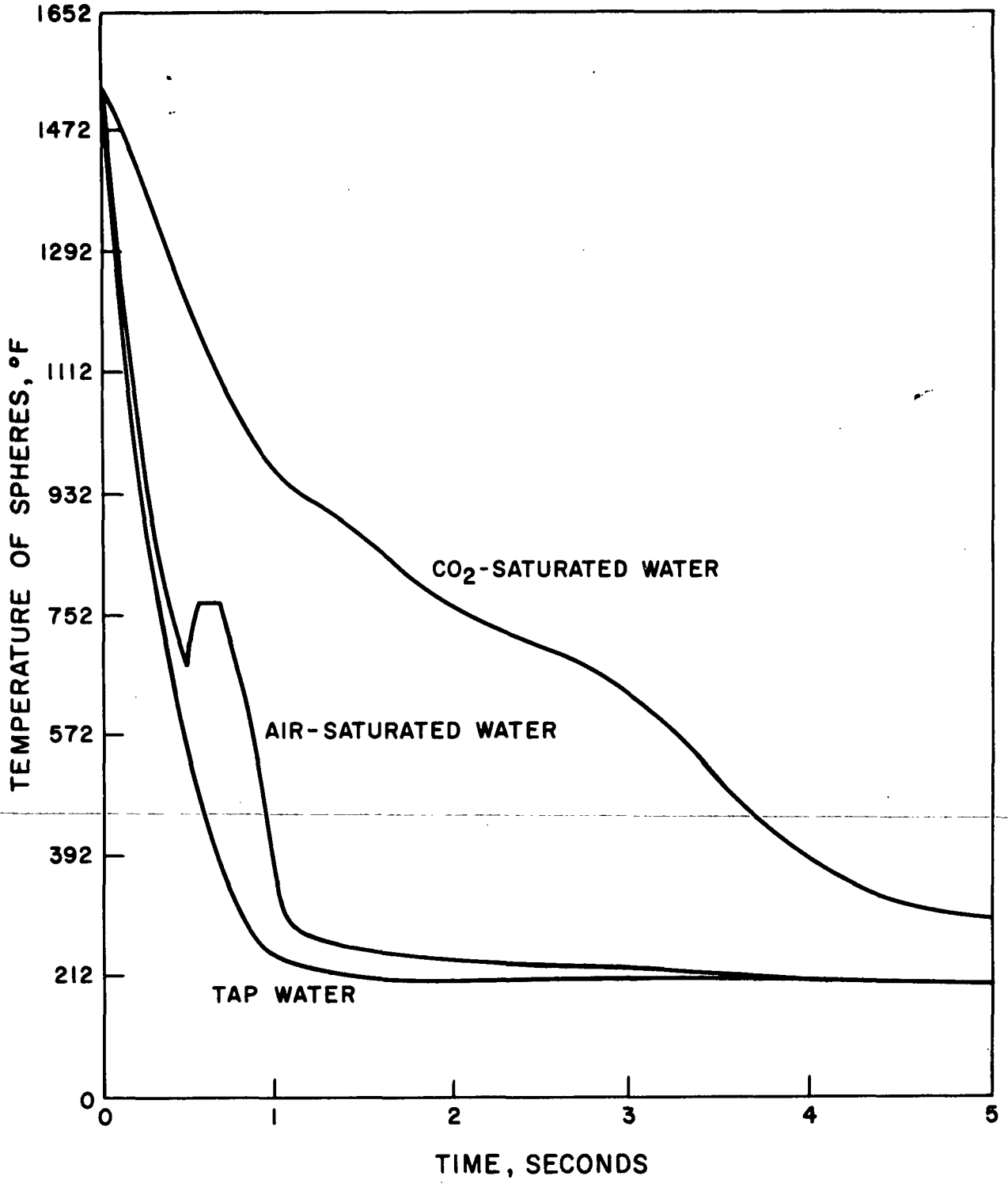
CENTER COOLING CURVES FOR 0.5" DIAMETER
STEEL CYLINDERS IN WATER
AT DIFFERENT TEMPERATURES
BY FRENCH[2]

FIGURE NO. 2



COOLING CURVES FOR STEEL CYLINDERS IN WATER CONTAINING DISSOLVED SOLIDS BY FRENCH [2]

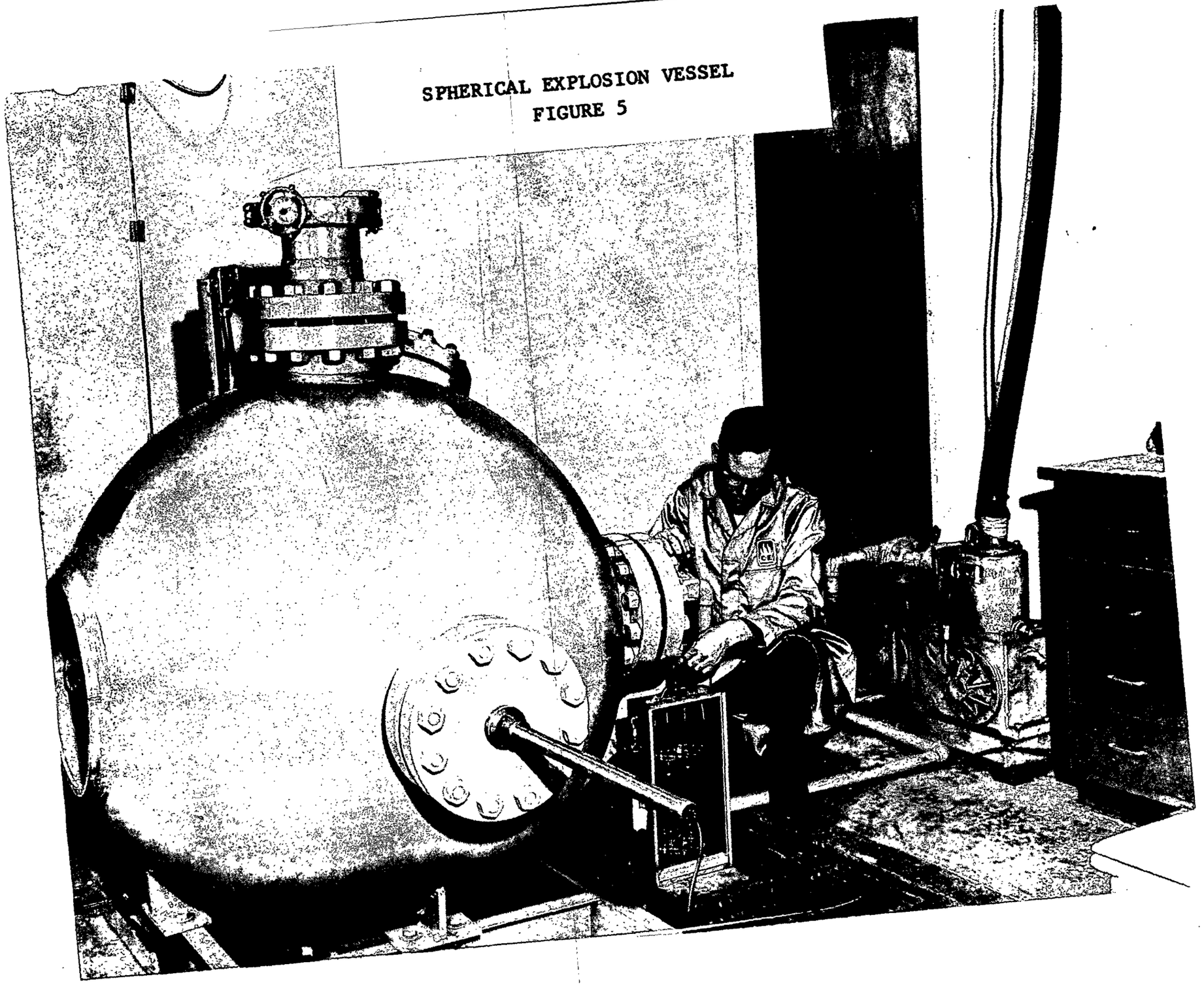
FIGURE NO. 3

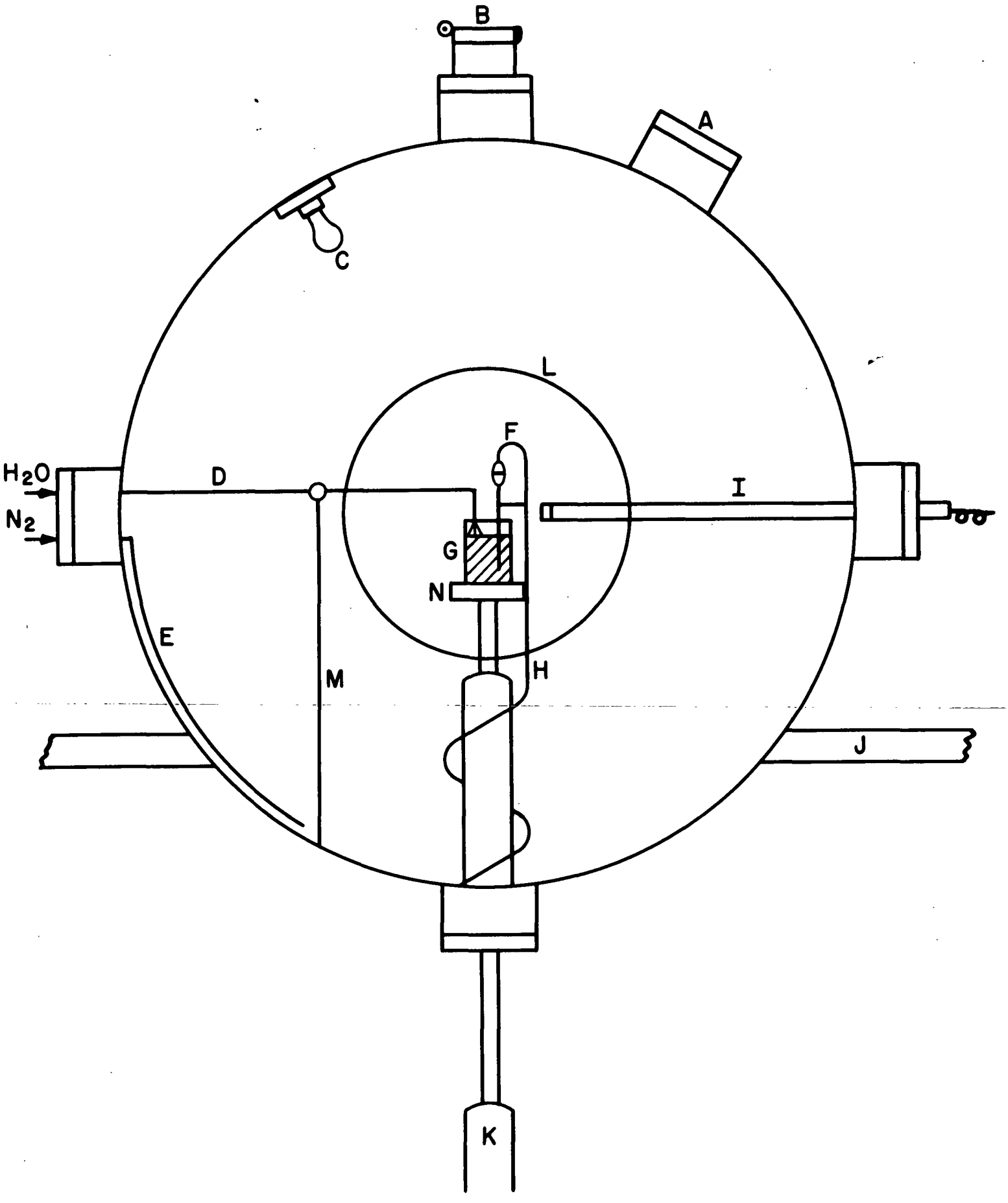


SURFACE COOLING CURVES FOR 1" DIAMETER STEEL SPHERES IN WATER CONTAINING DISSOLVED GASES BY FRENCH [2]

FIGURE NO. 4

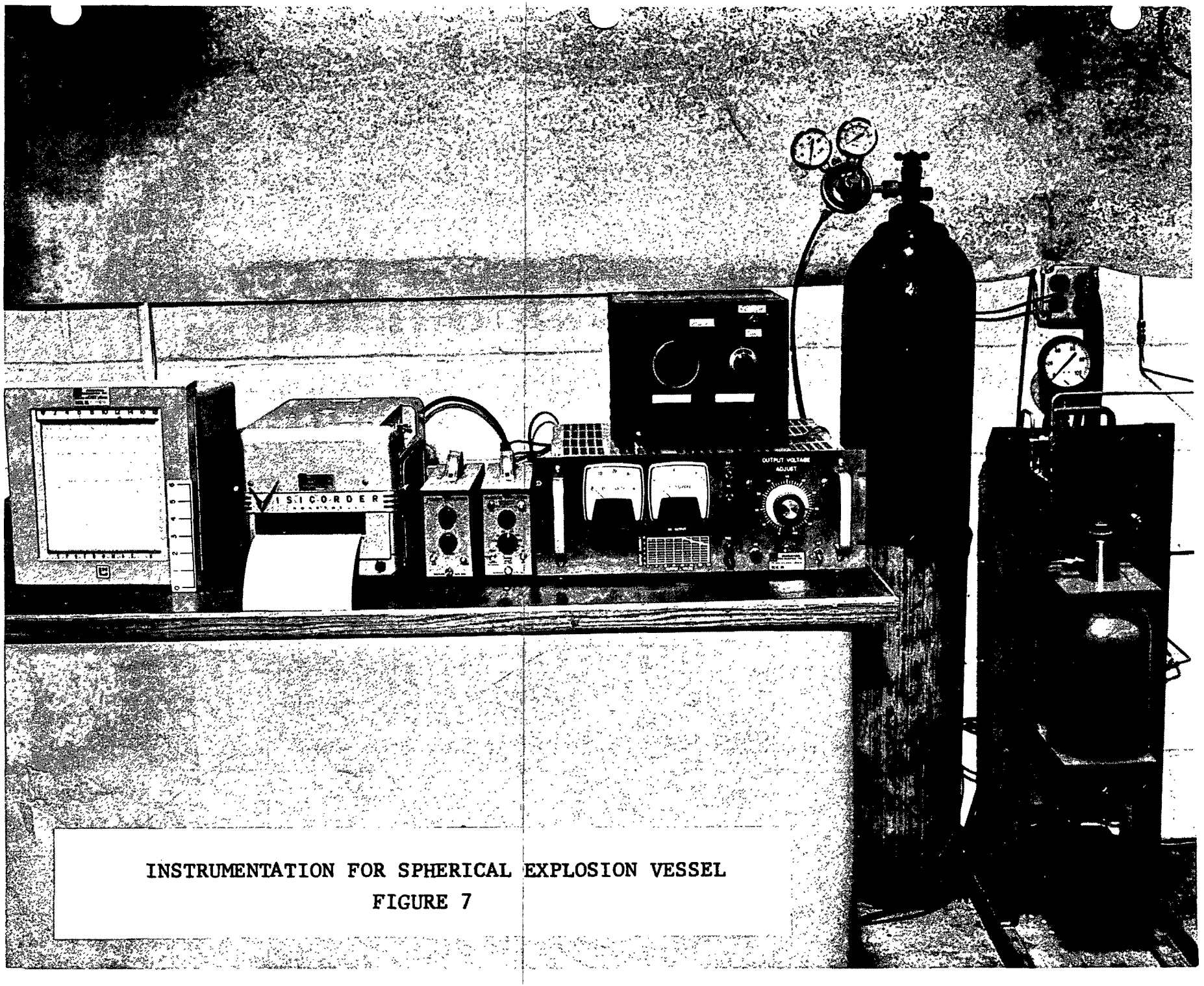
SPHERICAL EXPLOSION VESSEL
FIGURE 5





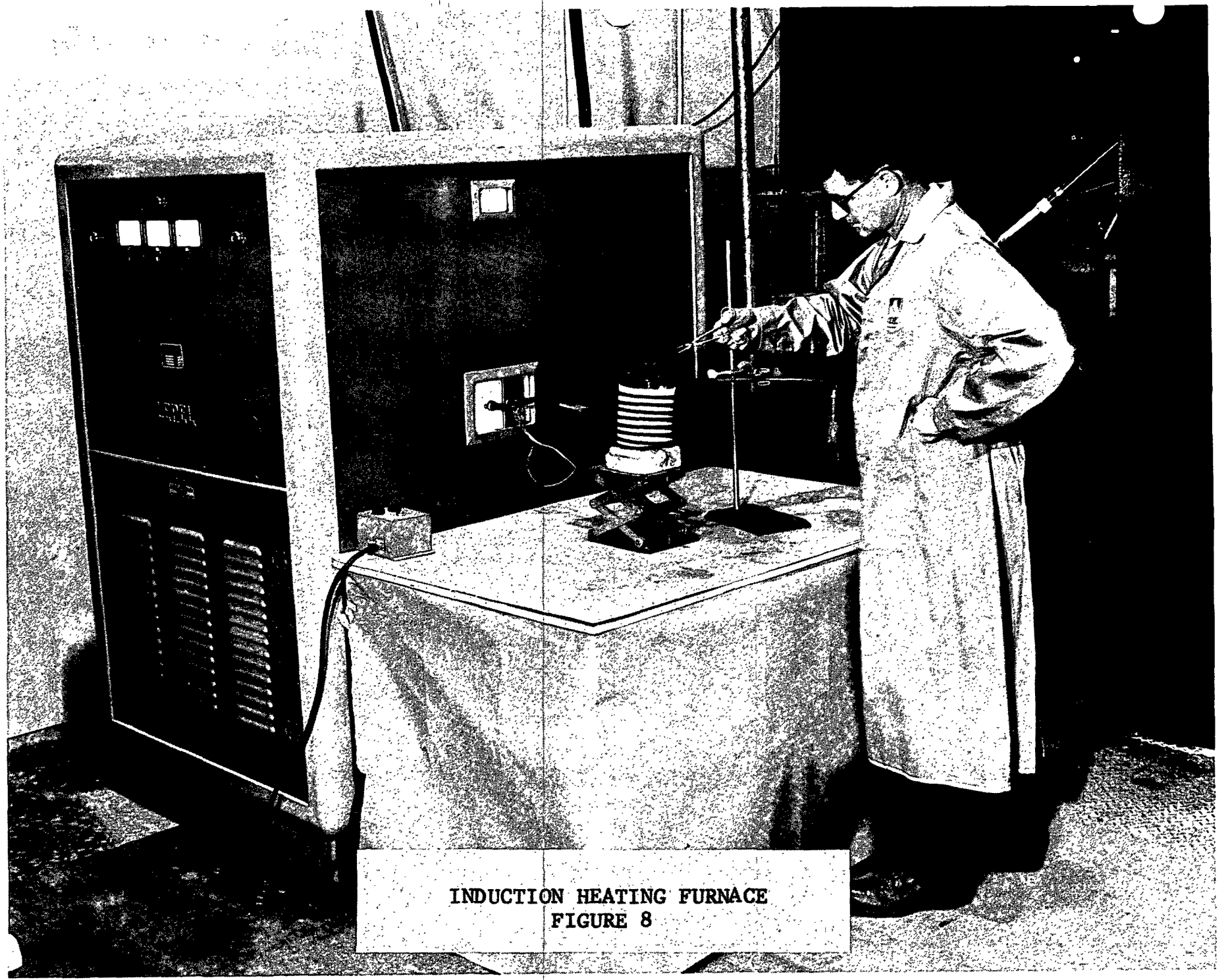
SPHERICAL EXPLOSION VESSEL

FIGURE NO. 6

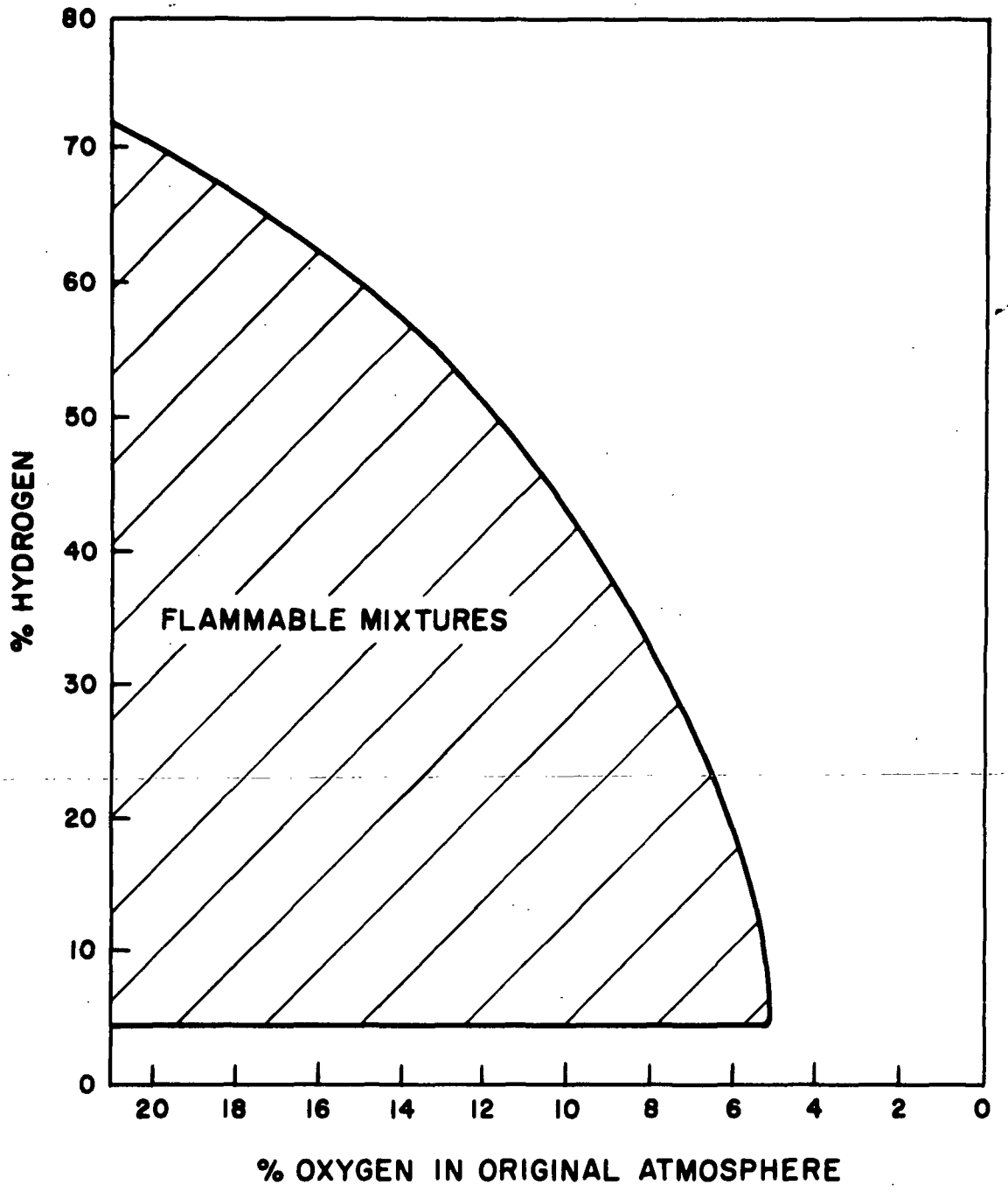


INSTRUMENTATION FOR SPHERICAL EXPLOSION VESSEL

FIGURE 7



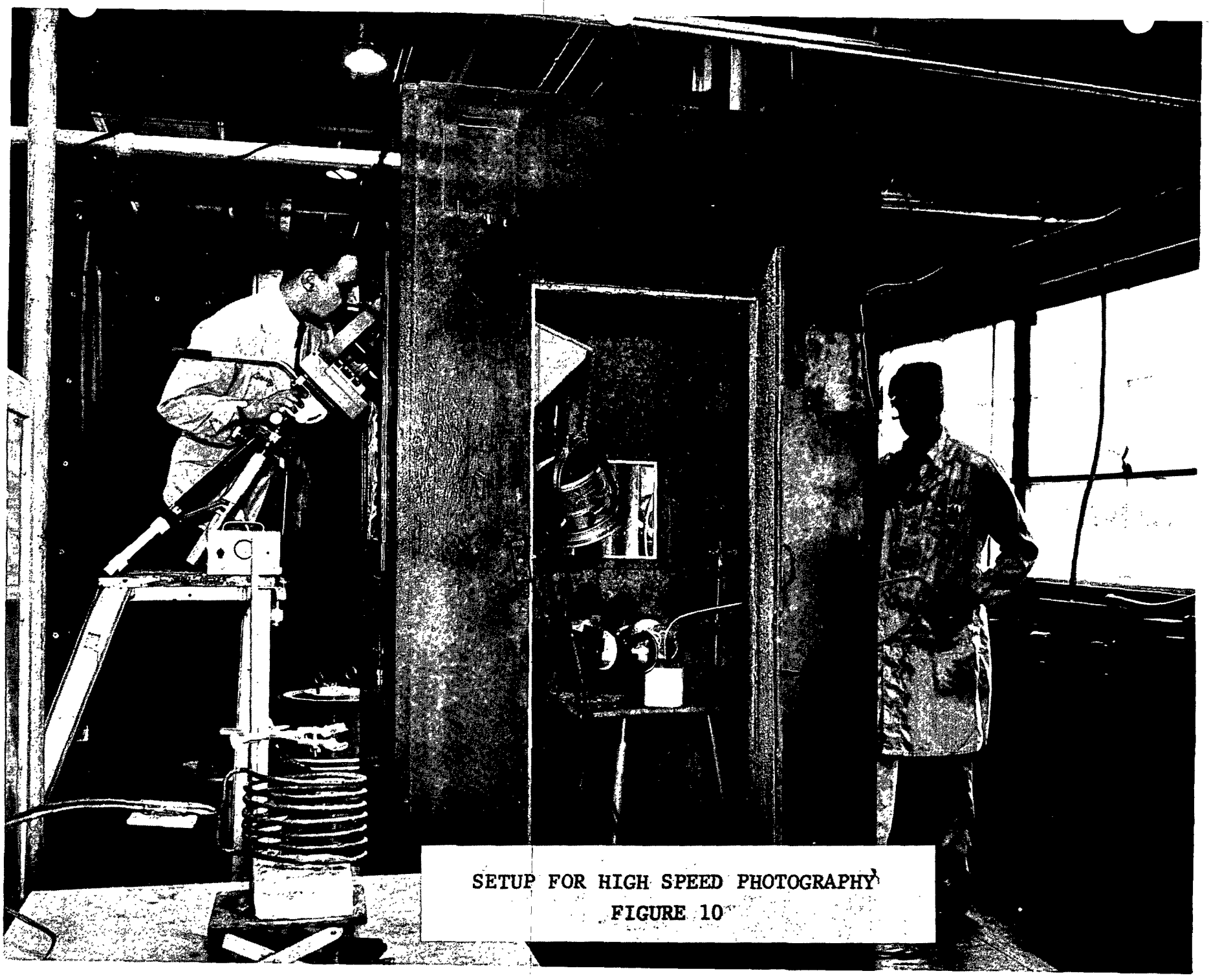
INDUCTION HEATING FURNACE
FIGURE 8



FLAMMABILITY LIMITS * OF HYDROGEN
IN NITROGEN - AIR MIXTURES

FIGURE NO. 9

* DATA FROM U.S. BUREAU OF MINES
BULLETIN 503, PAGE 20.

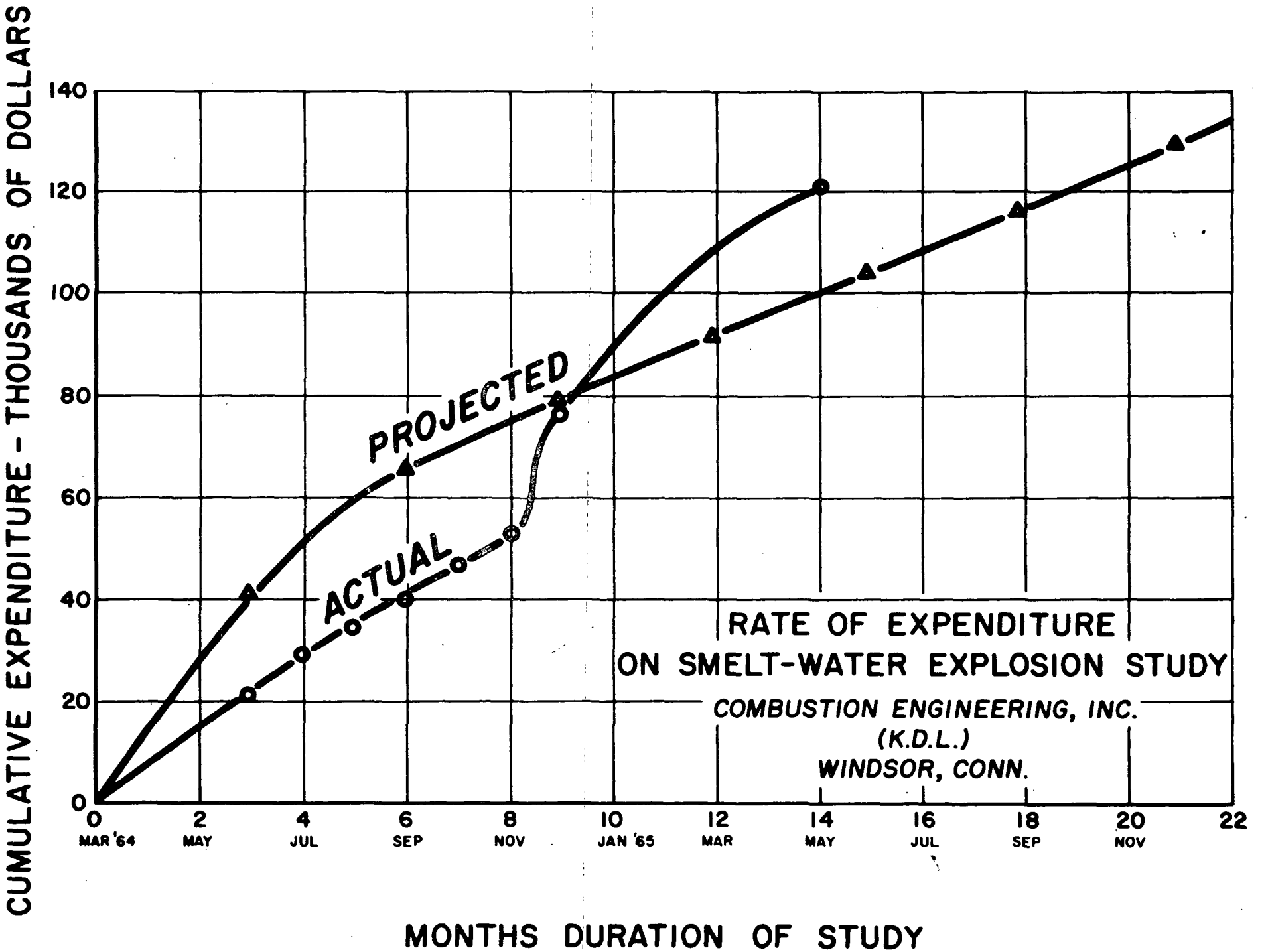


SETUP FOR HIGH SPEED PHOTOGRAPHY

FIGURE 10

PICTURES OF A SMELT-WATER EXPLOSION TAKEN AT 4500 FRAMES PER SECOND

FIGURE 11


CUMULATIVE EXPENDITURE - THOUSANDS OF DOLLARS
140
120
100
80
60
40
20
0
PROJECTED
ACTUAL
RATE OF EXPENDITURE
ON SMELT-WATER EXPLOSION STUDY
COMBUSTION ENGINEERING, INC.
(K.D.L.)
WINDSOR, CONN.
0 MAR '64
2 MAY
4 JUL
6 SEP
8 NOV
10 JAN '65
12 MAR
14 MAY
16 JUL
18 SEP
20 NOV
22
MONTHS DURATION OF STUDY

COMPUTER CALCULATIONS OF HEAT TRANSFER DURING SMELT ENCAPSULATION

MECHANICAL RESEARCH SECTION, KDL

A current theory of the cause of smelt-water explosions in Kraft chemical recovery units is that of the encapsulation mechanism. This theory states that when a quantity of water is injected beneath the surface of molten smelt, some of the smelt freezes around the water. This solid capsule of smelt confines the water to a given volume while the water receives heat from the capsule. Heating the water causes its pressure to increase until the capsule bursts causing an explosion.

To establish unquestionable validity of the encapsulation theory several conditions must be known. Some of these conditions can at best only be estimated. These include actual values for water volume, thermal resistance between the water-smelt interface, and the thickness of a vapor blanket if present between the water and smelt. Instead of the uncertain values of these conditions, a range of arbitrary values for each condition can be chosen within which the encapsulation mechanism theory is valid.

A conduction heat transfer program has been developed for a computer to determine what heat transfer rates occur in a water-smelt encapsulation model and how various conditions affect the heat transfer rates. The method used by the computer program considers the smelt as a series of concentric spherical shells with water in the center of the shells as shown in Figure 1.

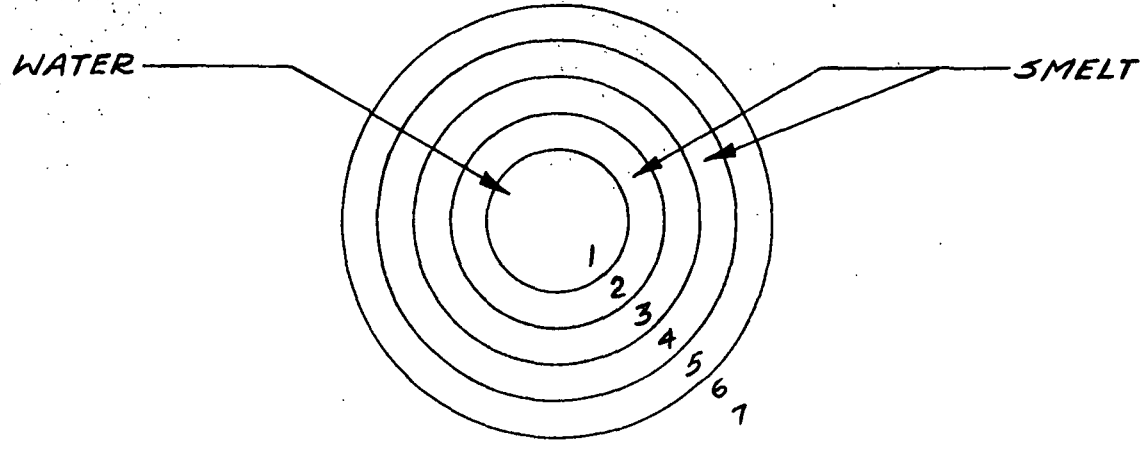


Figure 1 - Computer model of water in smelt.

The computer program calculates, by conduction heat transfer, the temperature of the water and each shell at successive time intervals for given initial conditions. Typical results of a computer solution are shown in Figure 2. A detailed discussion of the calculation procedure is given in Appendix I.

The temperature solution given by the computer has several uses:

1. The thickness of the solid smelt capsule at any time can be determined from the number of smelt shells having a temperature below the melting point of the smelt.

2. The pressure increase of the encapsulated water can be determined from the calculated water temperature increase.

3. The stress imposed on the solid smelt capsule by the pressurized water can be determined from the capsule thickness and water pressure.

The solutions obtained from the program must be coupled with tests run in the lab with actual smelt explosions. For example, several lab tests showed that an explosion occurred 30 milliseconds after 3 cc of 80°F water was injected into 1600°F smelt. In this case the unknown conditions required for a computer solution are the water volume in a given capsule, water-smelt interface thermal resistance, and presence of a steam blanket. A range of variations for each condition was chosen to determine how each would affect the heat transfer.

Effect of Encapsulated Water Volume

The maximum water volume possible in a single capsule in this case is 3 cc, but the 3 cc injection could break into a group of smaller volumes forming separate capsules. Figures 3, 4 and 5 show the effect of encapsulated water volume on water temperature increases, capsule thickness, and stress imposed on the capsule. Figure 3 shows that after 30 milliseconds (the induction period) the temperature increase of 0.3 cc of encapsulated water is 60°F while the temperature increase of 3 cc is only 20°F. The magnitude of the pressure increase in psi caused by this water temperature increase is 100 times the temperature increase. The pressure in a 0.3 cc encapsulated volume of water is 3 times as high as the pressure in a 3.0 cc volume. Figure 4 shows that variation of encapsulated water volume has little effect on the solid capsule thickness.

Figure 5 shows the strength required by the 0.3 cc capsule to contain the pressurized water is greater than the strength required by the 3 cc capsule because of the higher pressure increase of the 0.3 cc capsule. Yield stress of the solid smelt, while unknown, would be the same for each volume. This means that 3.0 cc of water would require a longer period of time to reach yield stress and explode than would 0.3 cc.

Effect of Vapor Blankets

A vapor blanket may exist between the encapsulated water and smelt, which would retard heat transfer. Figure 6 shows the effect of various vapor blanket thicknesses on the water temperature increase. A thickness of 0.0003 inch gives a water temperature increase of 20°F at 30 milliseconds while no vapor blanket gives a water temperature increase of 60°F. Also the vapor blanket is a compressible volume which the encapsulated water can expand into. Thus a vapor blanket would greatly decrease a pressure rise of the encapsulated water. This would tend to prevent rupture of the smelt capsule. Figure 7 shows the effect of a vapor blanket on the solid smelt capsule growth. A blanket 0.0003 inches thick reduces the capsule thickness to one half the thickness when no blanket is present.

Effect of Heat Transfer Coefficients

The heat transfer coefficient between the water and smelt may have some value smaller than the infinitely large one used in the previous examples. The thermal capacitance of a vapor blanket is negligible which means that the blanket can be considered as a finite heat transfer coefficient. Figures 6 and 7 show the effect of various vapor blanket thicknesses, which could also be considered as heat transfer coefficients in the range of 500 to 900 BTU/hr-ft^2-F, on water temperature increase and capsule thickness. Since there is no compressible volume when a heat transfer coefficient is used in place of a vapor blanket, the pressure increase in psi of the water is 100 times the water temperature increase. Figure 8 shows the effect on required capsule strength caused by various heat transfer coefficients. A reduction of the heat transfer coefficient reduces both the water temperature increase and the capsule thickness increase. Both of these effects oppose each other in determining the required capsule strength. This makes the required capsule strength in this range of heat transfer coefficients one half the required strength for an infinite coefficient of heat transfer.

Effect of Injected Water Temperatures

Other experiments have shown that injecting water at temperatures higher than 80°F into smelt decreases or prevents explosions. For instance, water injected at 176°F will cause an explosion while water injected at 186°F will not cause an explosion. Figures 9, 10 and 11 show that the temperature of injected water has little effect on the heat transfer results. However, water at the higher temperatures would tend to form a vapor blanket more easily than at the lower temperatures. The formation of any vapor blanket greatly changes the results as shown in Figures 6 and 7.

Effect of Initial Smelt Temperature

Other tests have also shown the temperature of the smelt has a significant effect on explosions. Injections into smelt above 1700°F have resulted in no explosions. Figure 12 shows that the initial smelt temperature has a small effect on water temperature increase. Figure 13 shows that the initial smelt temperature has a great effect on the capsule thickness with 1800°F smelt having a capsule thickness one half the thickness of that obtained with 1500°F smelt. This great difference in capsule thickness gives a significant change in required shell strength as shown in Figure 14. Smelt having a temperature of 1800°F requires a strength which is 50% greater than that required for 1600°F smelt. This means that at high smelt temperatures, a capsule may be ruptured before it develops significant internal pressure, which would prevent an explosion.

Effect of Specific Heat of Injected Fluid

The academic question of what would happen if alcohol or another fluid having a different specific heat than water was injected into smelt, has arisen. Figure 15 shows what temperature increase would be experienced by various fluids having different specific heats. As would be expected, a greater temperature increase occurs for fluids having lower specific heats. Fluids with a lower specific heat than water tend to be more volatile than water and would tend to form vapor blankets more readily than water which would have more influence on the required shell strength than the increased temperature rise. Figure 16 shows that a change of specific heat has a negligible effect on the capsule thickness.

Conclusions

The conditions which by themselves have significant effects on the strength required by the solid smelt capsule to contain the pressurized water are:

1. Encapsulated Water Volume - the required strength increases as the volume decreases.

2. Presence of a Vapor Blanket Between the Water and Smelt - a vapor blanket retards the pressure increase of the water and provides a compressible volume. Both of these decrease the required strength. A vapor blanket might also prevent formation of a shell entirely by retarding heat transfer.

3. Smelt Temperature - the required strength increases as the smelt temperature is increased.

The temperature of the injected water by itself has no significant effect on capsule strength required to contain the water. While these above conditions have effects by themselves, they may also cause others to occur which make them more or less interdependent on each other. Therefore, while water temperature by itself has no significant influence on required capsule strength it may cause formation of a vapor blanket which does have a significant effect on the required strength.

Acknowledgements

The author of this report is grateful for the work of programing this problem for the computer done by Mr. A. R. Sireci. The author is also grateful for the work done by Mr. B. Bowman who drew up figures and made calculations.

B. C. Teigen

BCT:MJ

COMBUSTION ENGINEERING, INC.

CHANGE OF STATE HEAT TRANSFER

TIME - SEC.	DTAUC
0.00200	0.

	NODE NO.	TEMPERATURE
Water	1	87.3065
↓	2	1466.0894
Smelt	3	1594.4382
	4	1599.8599
	5	1599.9972
	6	1599.9995
	7	1599.9997
	8	1599.9998
	9	1599.9998
	10	1599.9999
	11	1599.9999
	12	1600.0000
	13	1600.0000
	14	1600.0000
	15	1600.0000
	16	1600.0000
	17	1600.0000
	18	1600.0000
	19	1600.0000
	20	1600.0000
	21	1600.0000
	22	1600.0000

COMBUSTION ENGINEERING, INC.

CHANGE OF STATE HEAT TRANSFER

TIME - SEC.	DTAUC
0.00261	1.

	NODE NO.	TEMPERATURE
	1	89.4129
Melting	2	1430.0000
Temp	3	1590.6228
	4	1599.6748
	5	1599.9915
	6	1599.9991
	7	1599.9994
	8	1599.9996
	9	1599.9996
	10	1599.9997
	11	1599.9997
	12	1599.9998
	13	1599.9998
	14	1599.9999
	15	1599.9999
	16	1600.0000
	17	1600.0000
	18	1600.0000
	19	1600.0000
	20	1600.0000
	21	1600.0000
	22	1600.0000

COMBUSTION ENGINEERING, INC.

CHANGE OF STATE HEAT TRANSFER

TIME - SEC.	DTAUC
0.01857	2.

	NODE NO.	TEMPERATURE
	1	134.7307
	2	1004.2281
Melting	3	1430.0000
Temp	4	1561.9811
	5	1592.8963
	6	1598.8623
	7	1599.8423
	8	1599.9766
	9	1599.9921
	10	1599.9934
	11	1599.9943
	12	1599.9951
	13	1599.9958
	14	1599.9963
	15	1599.9968
	16	1599.9972
	17	1599.9977
	18	1599.9981
	19	1599.9986
	20	1599.9990
	21	1599.9995
	22	1600.0000

Figure 2. Computer Program Results

COMBUSTION ENGINEERING, INC.

CHANGE OF STATE HEAT TRANSFER

TIME - SEC.	DTAUC
0.04849	3.

	NODE NO.	TEMPERATURE
	1	186.4378
	2	748.1841
	3	1186.4871
Melting Temp	4	1430.0000
	5	1535.6048
	6	1577.6986
	7	1593.0167
	8	1598.0141
	9	1599.4819
	10	1599.8694
	11	1599.9608
	12	1599.9797
	13	1599.9832
	14	1599.9853
	15	1599.9873
	16	1599.9892
	17	1599.9911
	18	1599.9928
	19	1599.9946
	20	1599.9964
	21	1599.9982
	22	1600.0000

COMBUSTION ENGINEERING, INC.

CHANGE OF STATE HEAT TRANSFER

TIME - SEC.	DTAUC
0.09278	4.

	NODE NO.	TEMPERATURE
Water ↓ Smelt	1	238.4312
	2	640.1543
	3	999.5037
	4	1266.6569
Melting Temp	5	1430.0000
	6	1516.8894
	7	1561.2575
	8	1582.7834
	9	1592.8110
	10	1597.2040
	11	1598.9795
	12	1599.6423
	13	1599.8700
	14	1599.9428
	15	1599.9650
	16	1599.9724
	17	1599.9775
	18	1599.9823
	19	1599.9869
	20	1599.9914
	21	1599.9958
	22	1600.0000

Figure 2 cont.

Figure 3
VARIATION OF WATER TEMPERATURE INCREASE WITH TIME FOR VARIOUS WATER VOLUMES

T_{ow} = 80 F
T_{osmelt} = 1600 F
$h = \infty$

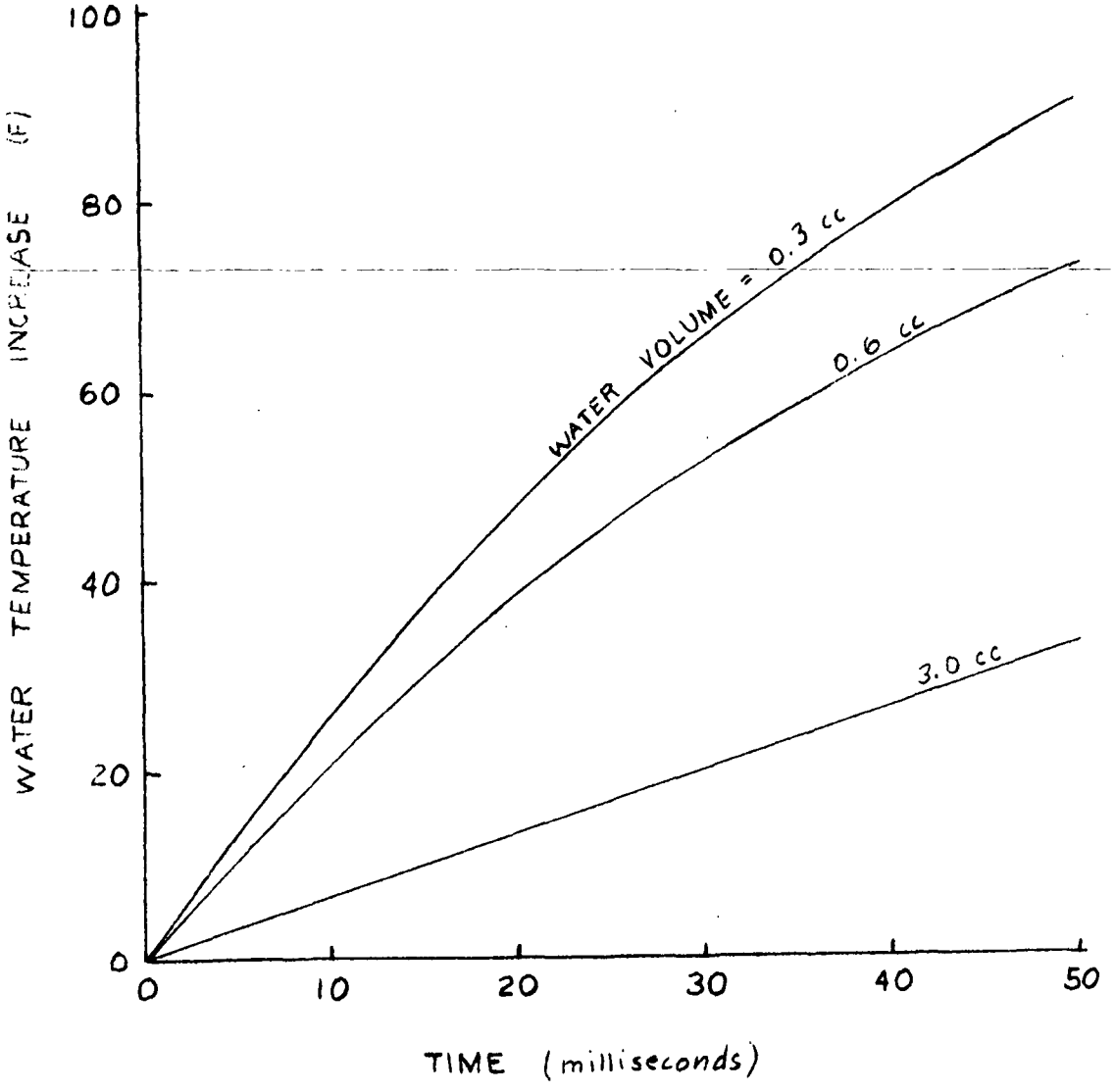


Figure 4
VARIATION OF SOLID SMELT CAPSULE THICKNESS WITH TIME FOR VARIOUS WATER VOLUMES

T_{ow} = 80F
T_{osmelt} = 1600 F
h = ∞

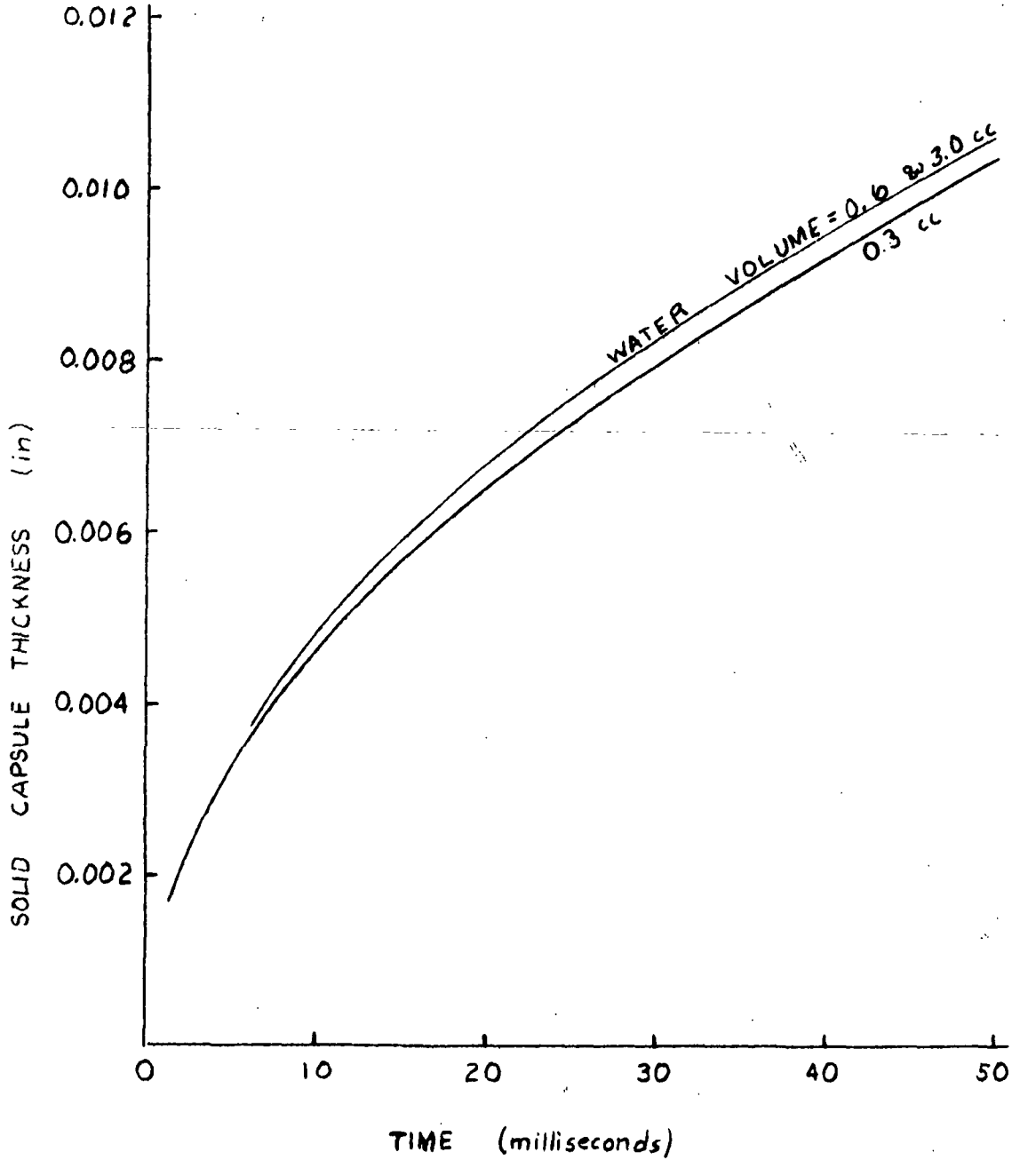


Figure 5
VARIATION OF STRESS IMPOSED ON SOLID CAPSULE WITH TIME FOR VARIOUS WATER VOLUMES

$T_{OW} = 80°F$

$T_{O_{SMELT}} = 1600°F$

$h = \infty$

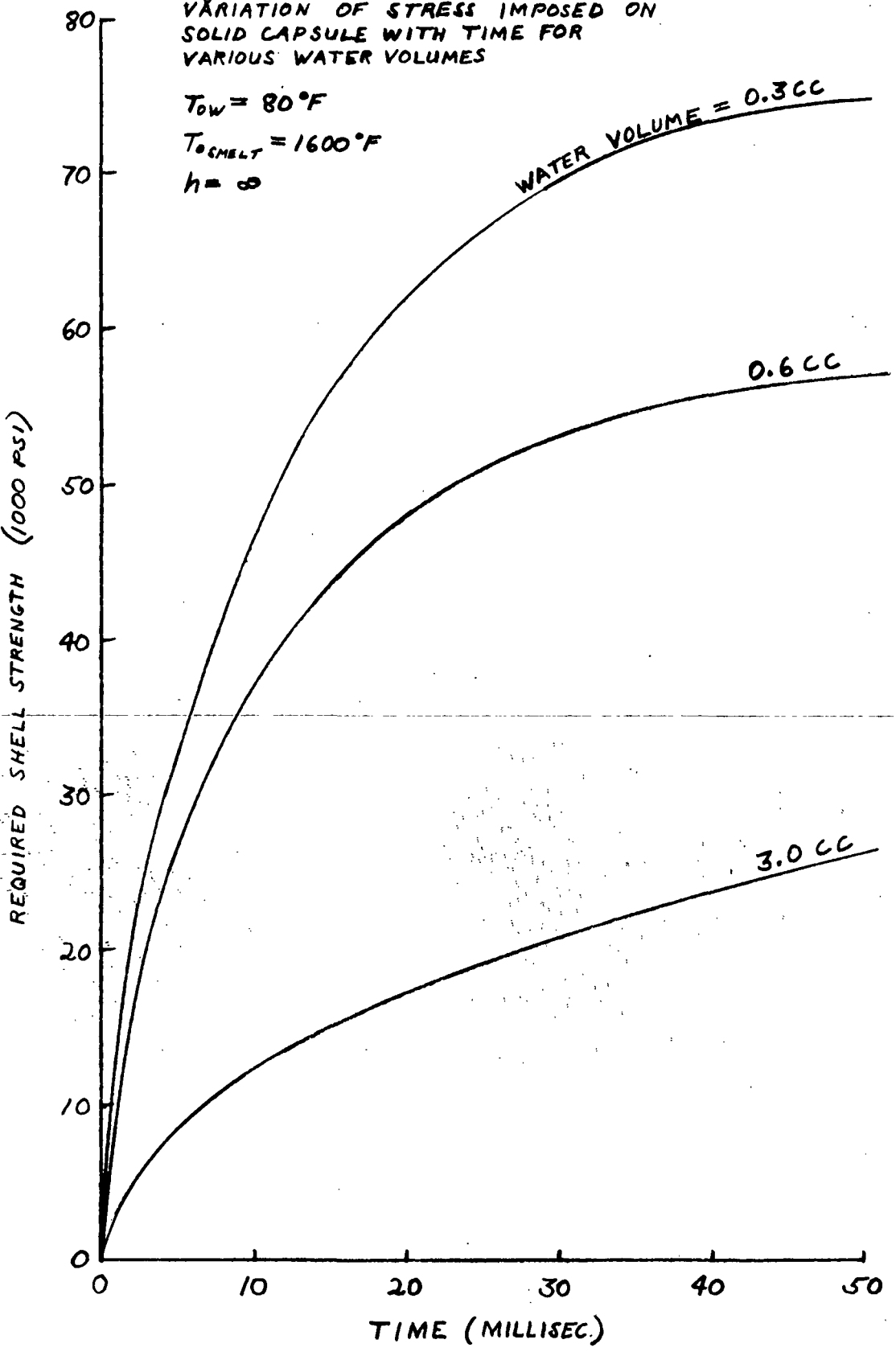


FIGURE 6.

AFFECT OF PRESENCE OF A VAPOR BLANKET ON ENCAPSULATED WATER TEMPERATURE

WATER TEMPERATURE INCREASE
VS
TIME

FOR DIFFERENT VAPOR BLANKET THICKNESSES OR FOR DIFFERENT WATER-SMELT CONVECTIVE HEAT TRANSFER COEFFICIENTS

V_W = 0.3 cc
T_{ow} = 80 F
T_{SMELT} = 1600 F

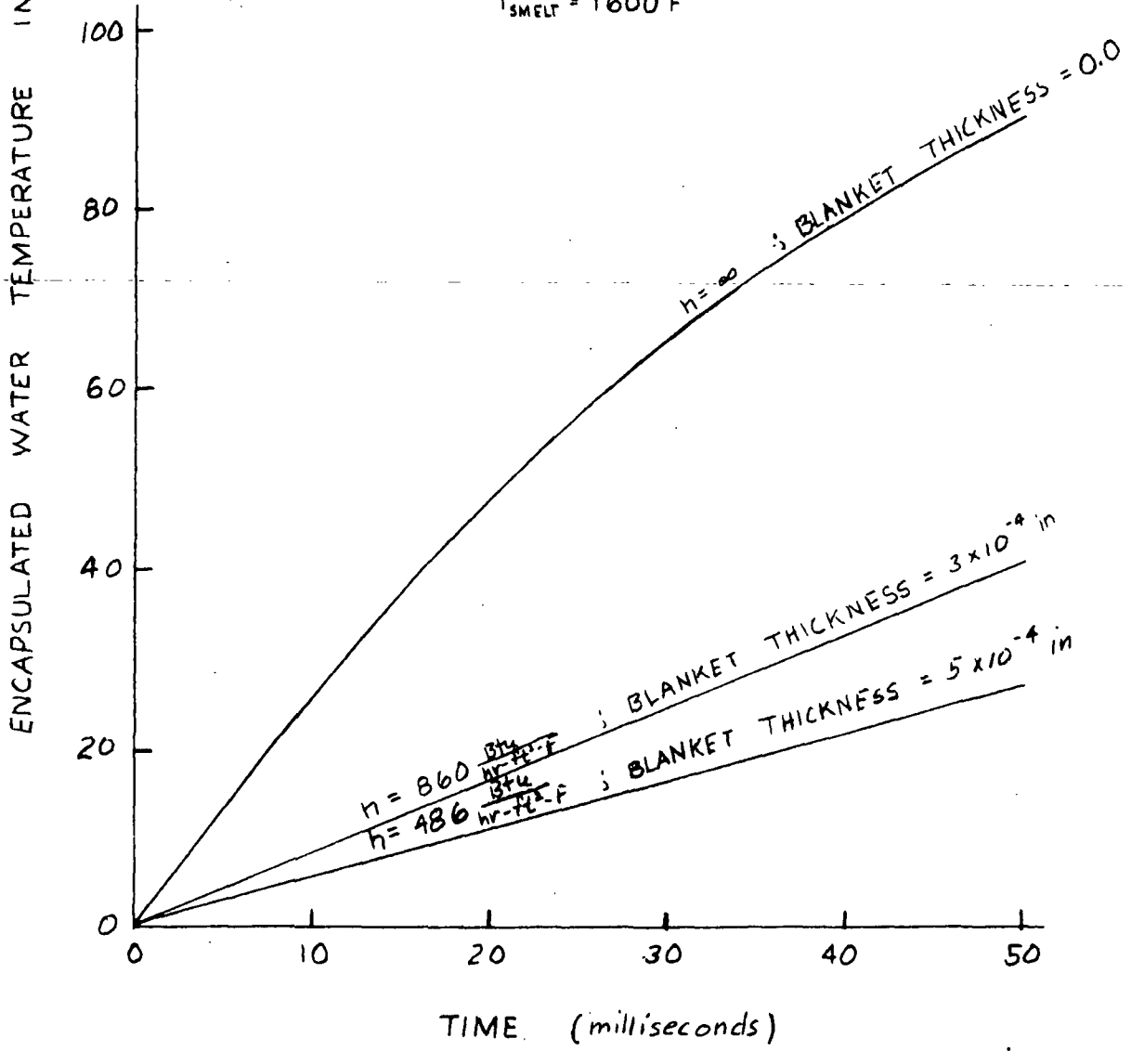


Figure 7
VARIATION OF SOLID SMELT CAPSULE THICKNESS WITH TIME FOR VARIOUS VAPOR BLANKET THICKNESSES OR VARIOUS WATER-SMELT HEAT TRANSFER COEFFICIENTS

V_w = 0.3 cc
T_{w_o} = 80 F
T_{SMELT} = 1600 F

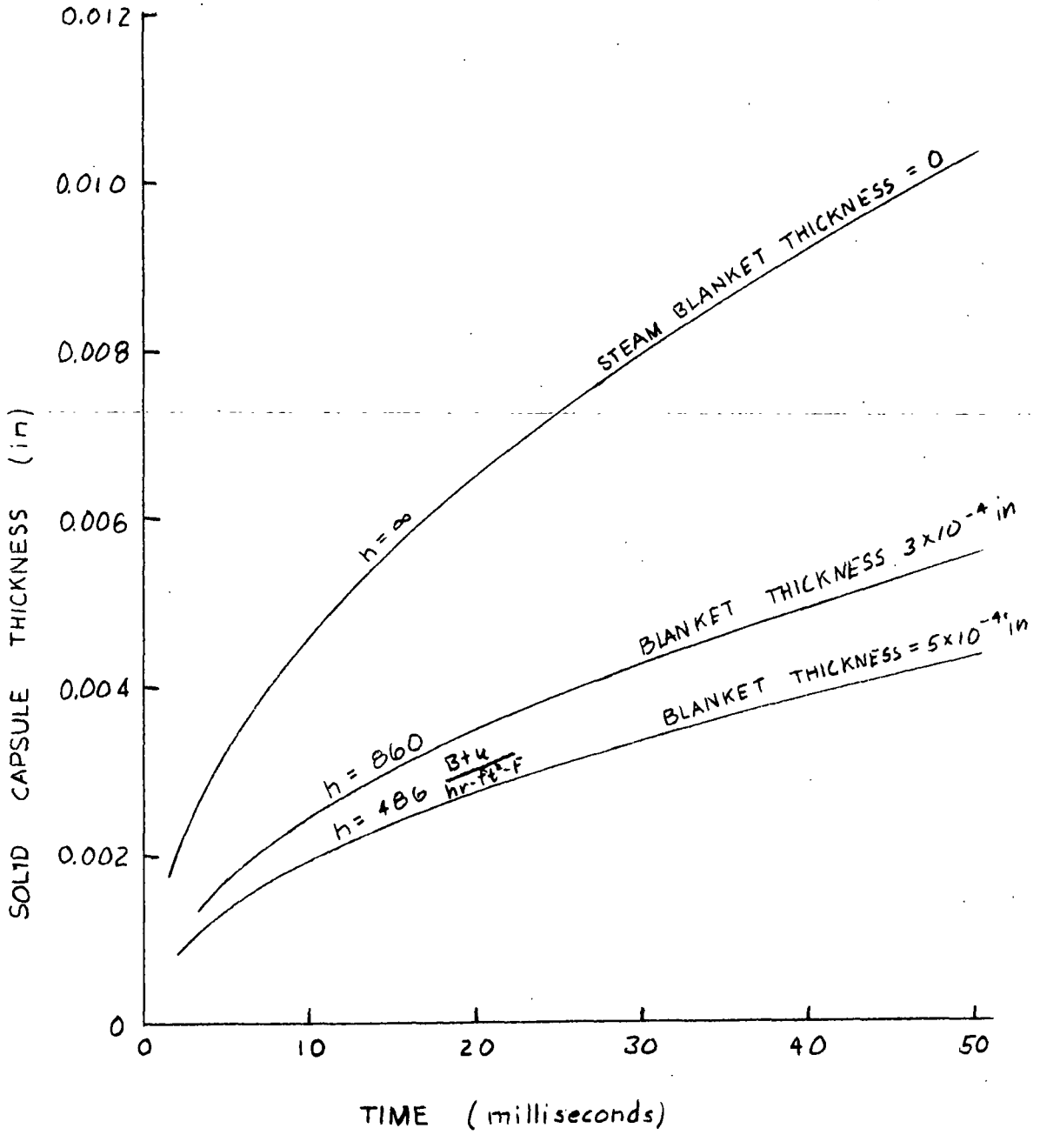


Figure 8.
VARIATION OF SOLID SHELL STRENGTH REQUIRED TO CONTAIN ENCAPSULATED WATER — STRENGTH vs TIME FOR VARIOUS WATER-SMELT HEAT TRANSFER COFFICIENTS

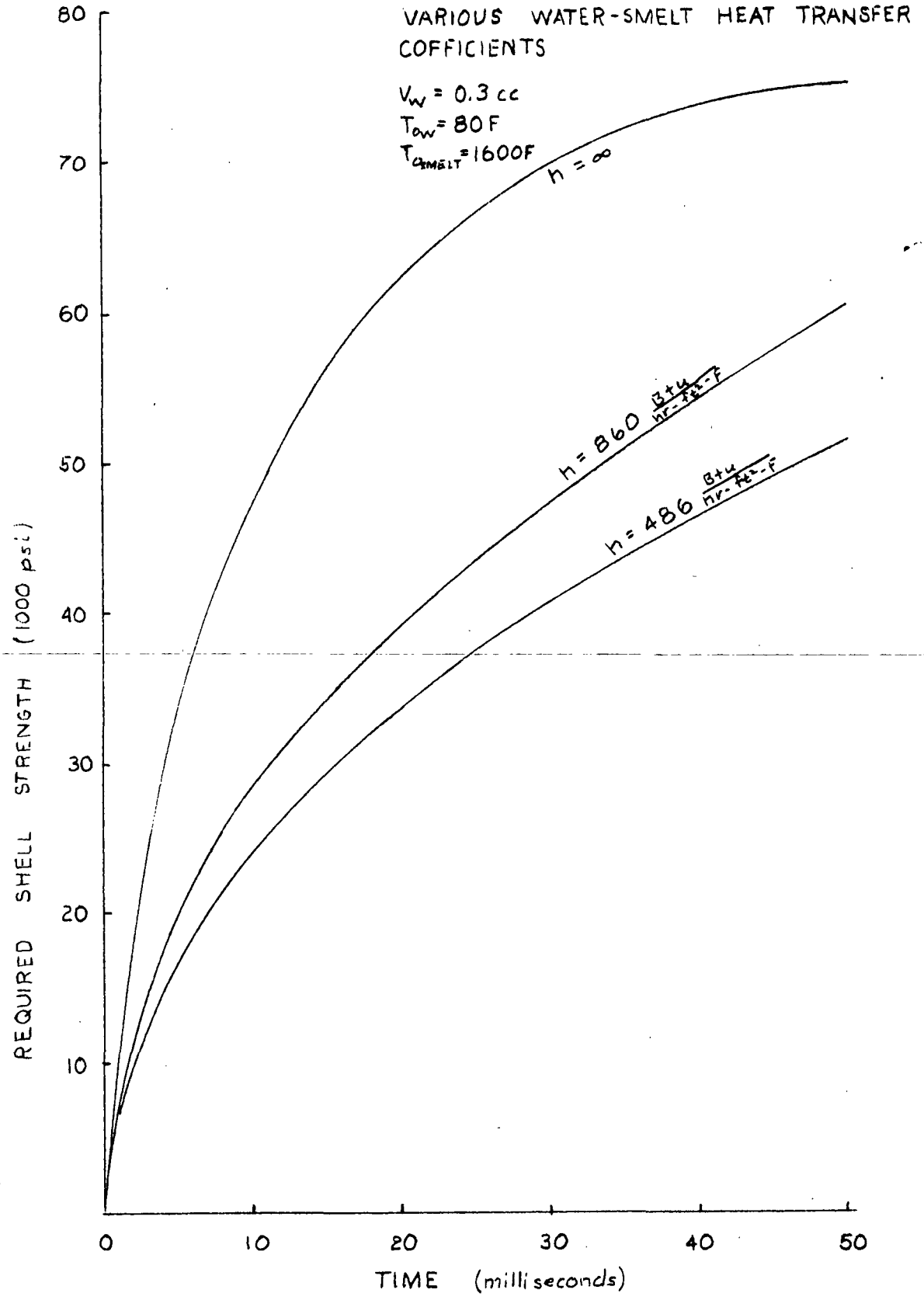


Figure 9
VARIATION OF SOLID SMELT CAPSULE THICKNESS WITH TIME FOR VARIOUS INITIAL WATER TEMPERATURES

V_w = 0.3 cc
T_{SMELT} = 1600
h = ∞

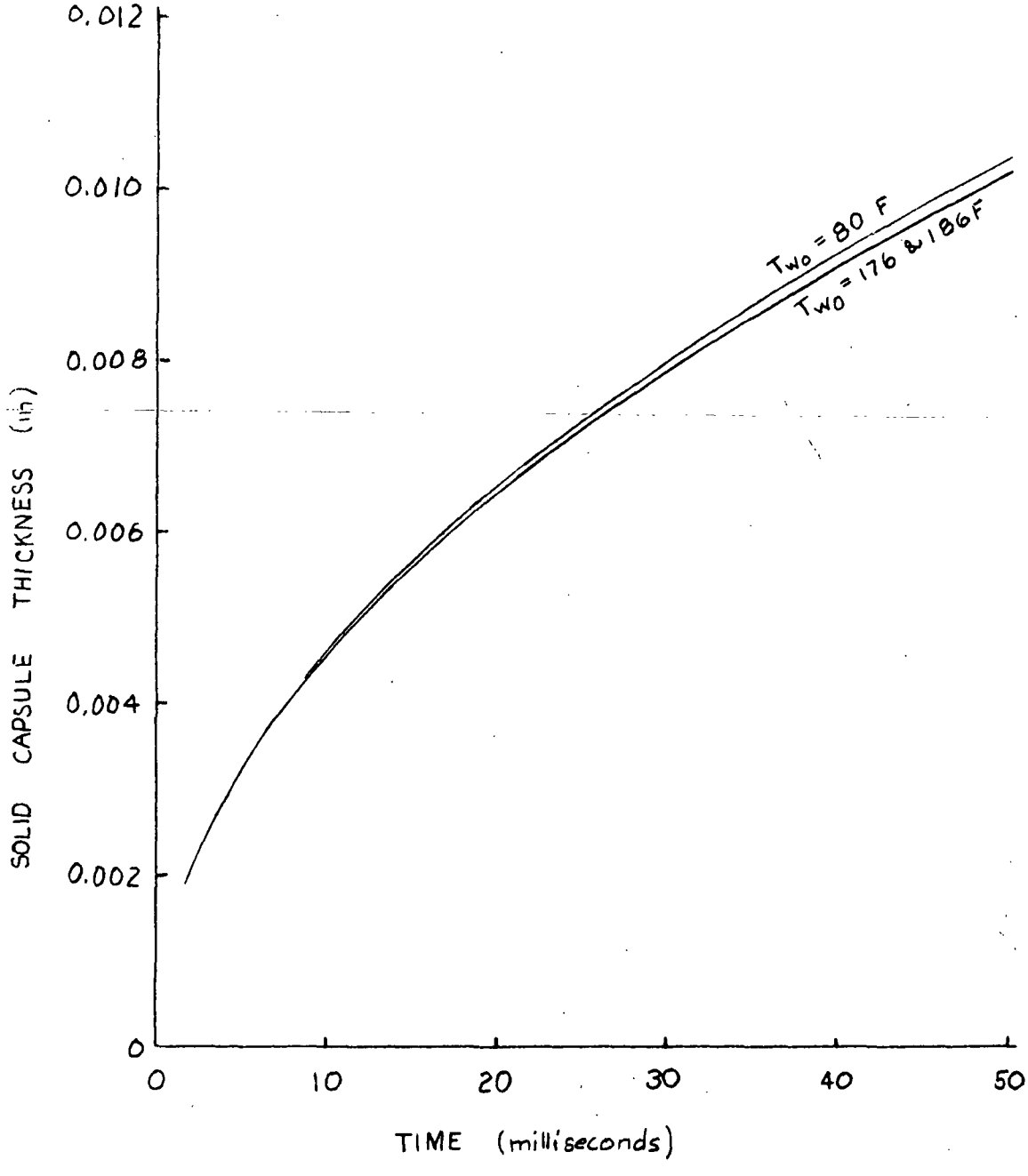
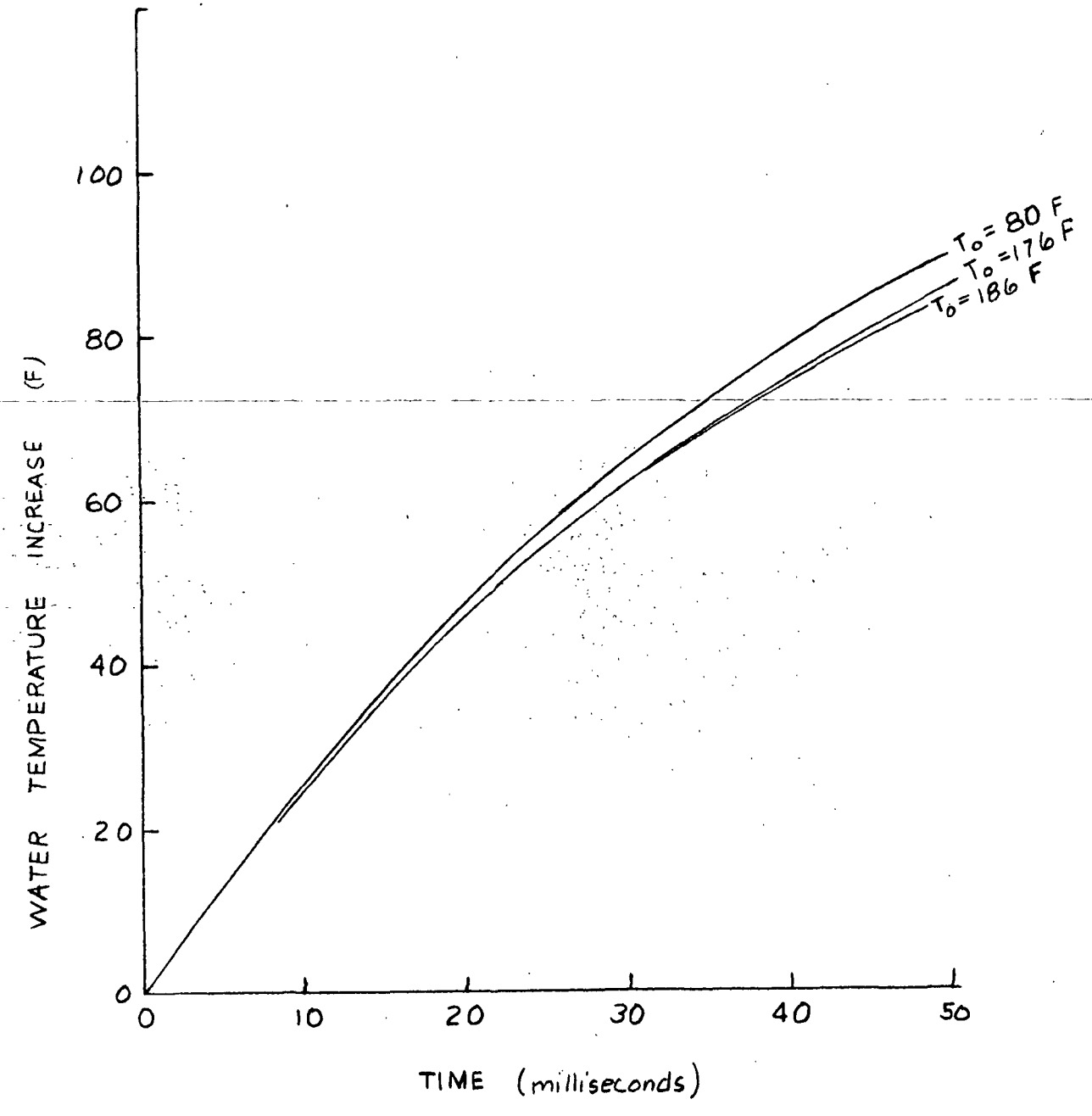


Figure 10

VARIATION OF WATER TEMPERATURE INCREASE WITH TIME FOR VARIOUS INITIAL WATER TEMPERAURUES

$V_W = 0.3$ cc
$T_{SMELT} = 1600$ F
$h = \infty$



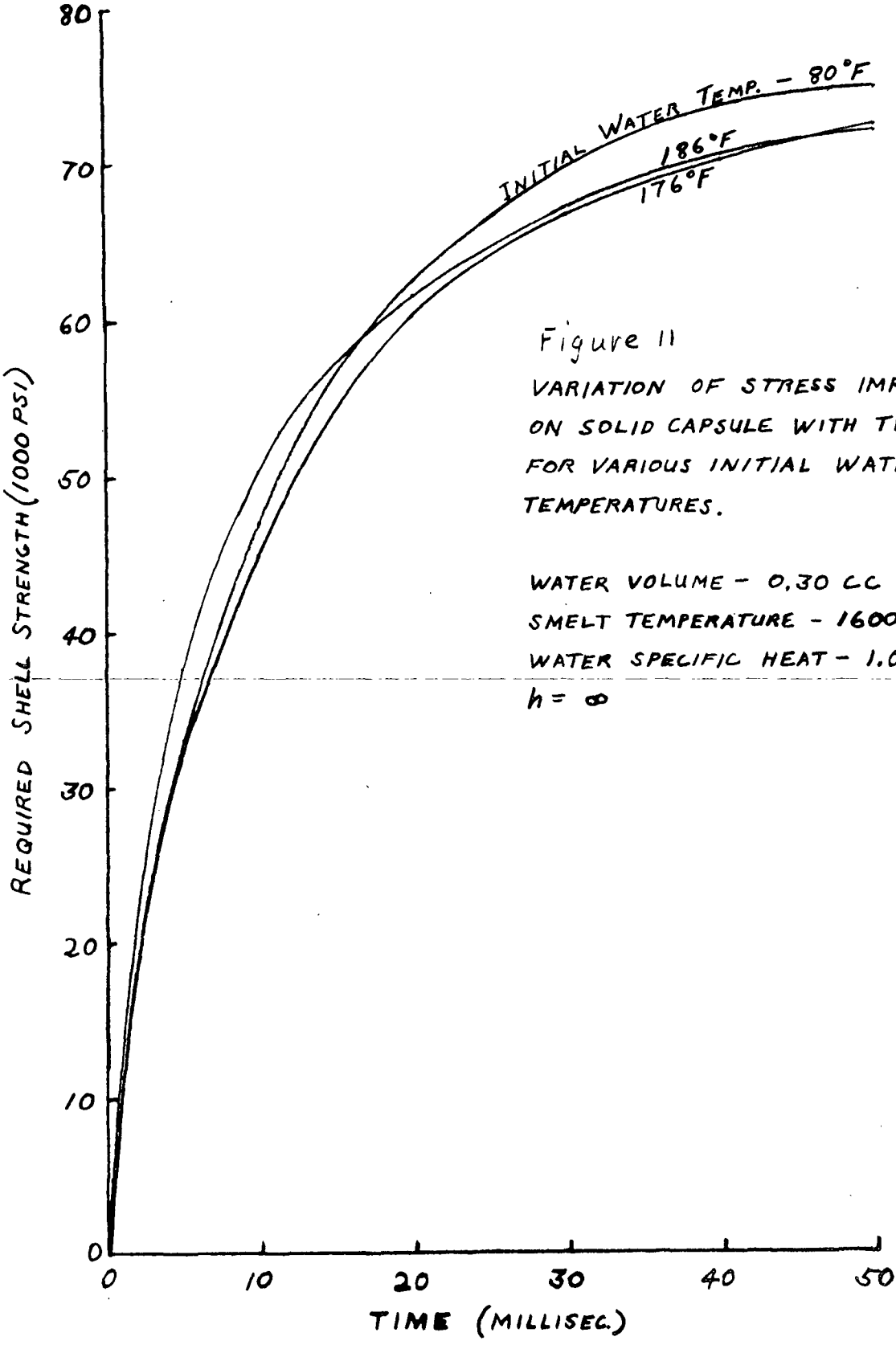


Figure 11

VARIATION OF STRESS IMPOSED ON SOLID CAPSULE WITH TIME FOR VARIOUS INITIAL WATER TEMPERATURES.

WATER VOLUME - 0.30 CC

SMELT TEMPERATURE - 1600°F

WATER SPECIFIC HEAT - 1.0 $\frac{BTU}{LB.-°F}$

$h = \infty$

Figure 12
VARIATION OF WATER TEMPERATURE INCREASE WITH TIME FOR VARIOUS INITIAL SMELT TEMPERATURES

$V_w = 0.3$ cc

$T_{ow} = 80$ F

$h = \infty$

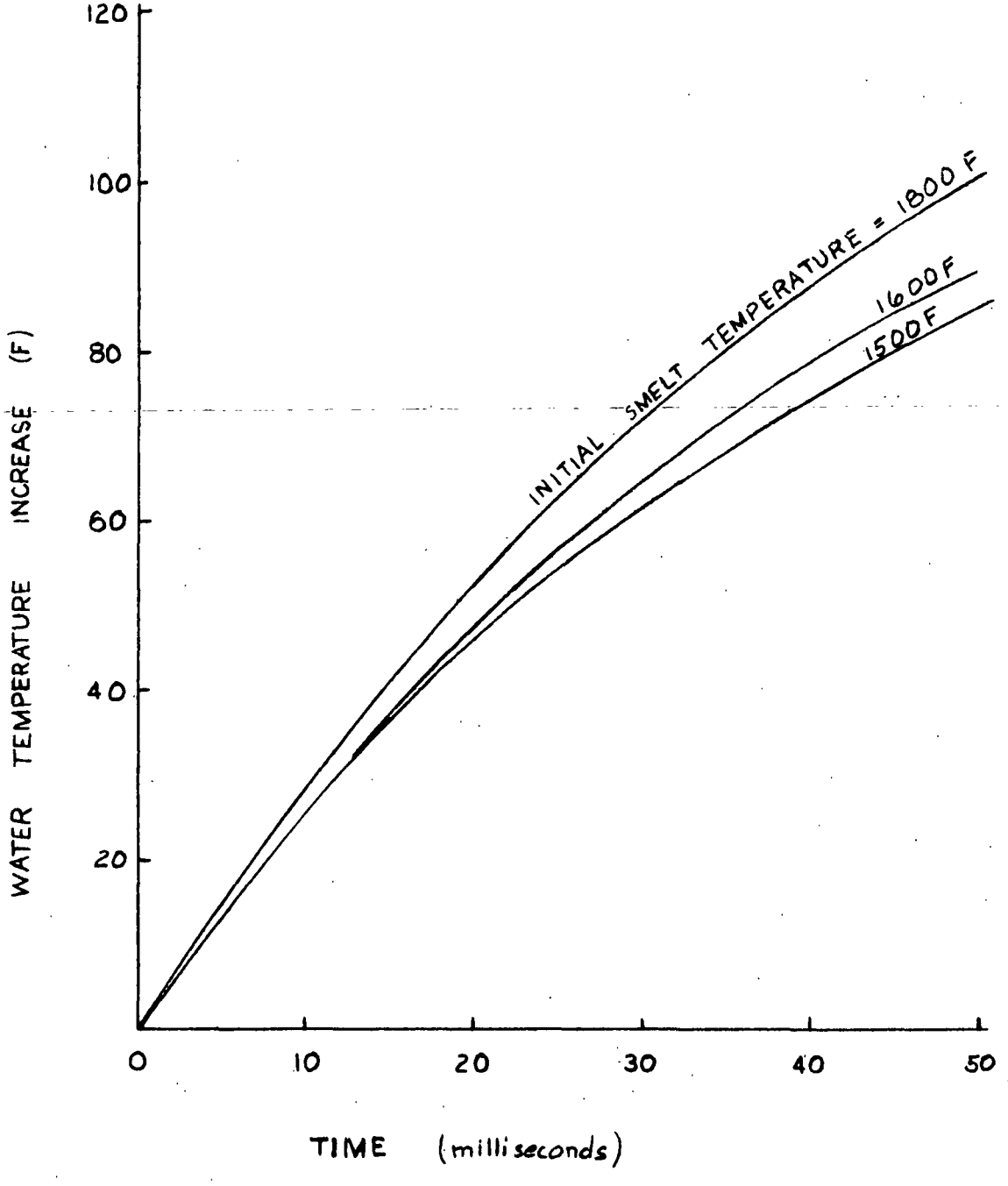


Figure 13
VARIATION OF SOLID SMELT CAPSULE THICKNESS WITH TIME FOR VARIOUS INITIAL SMELT TEMPERATURES

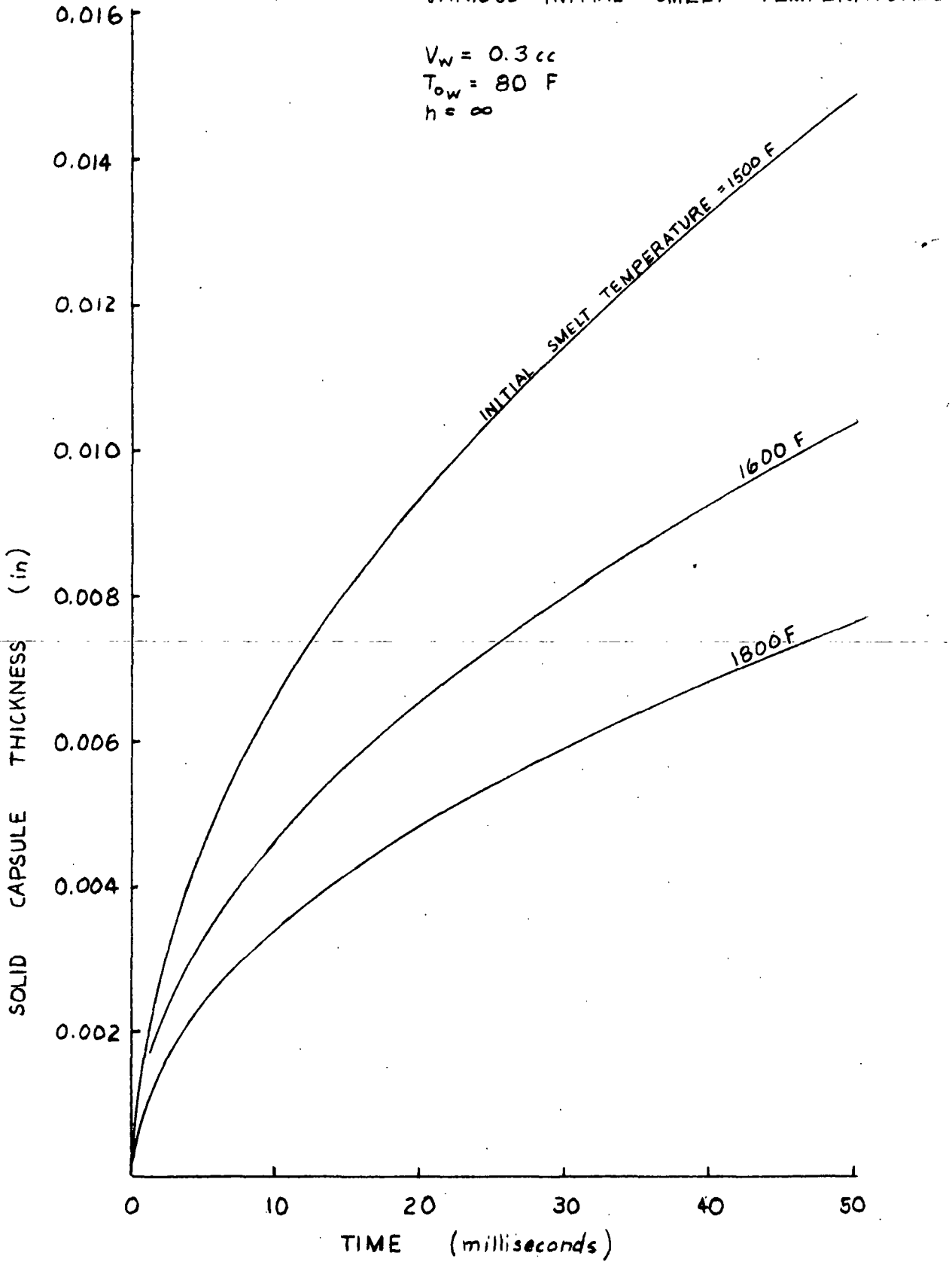


Figure 14

VARIATION OF STRESS IMPOSED ON SOLID CAPSULE WITH TIME FOR VARIOUS INITIAL SMELT TEMPERATURES

WATER VOLUME - 0.30 cc
WATER TEMPERATURE - 80 F
WATER SPECIFIC HEAT - 1.0 $\frac{Btu}{lb-F}$
$h = \infty$

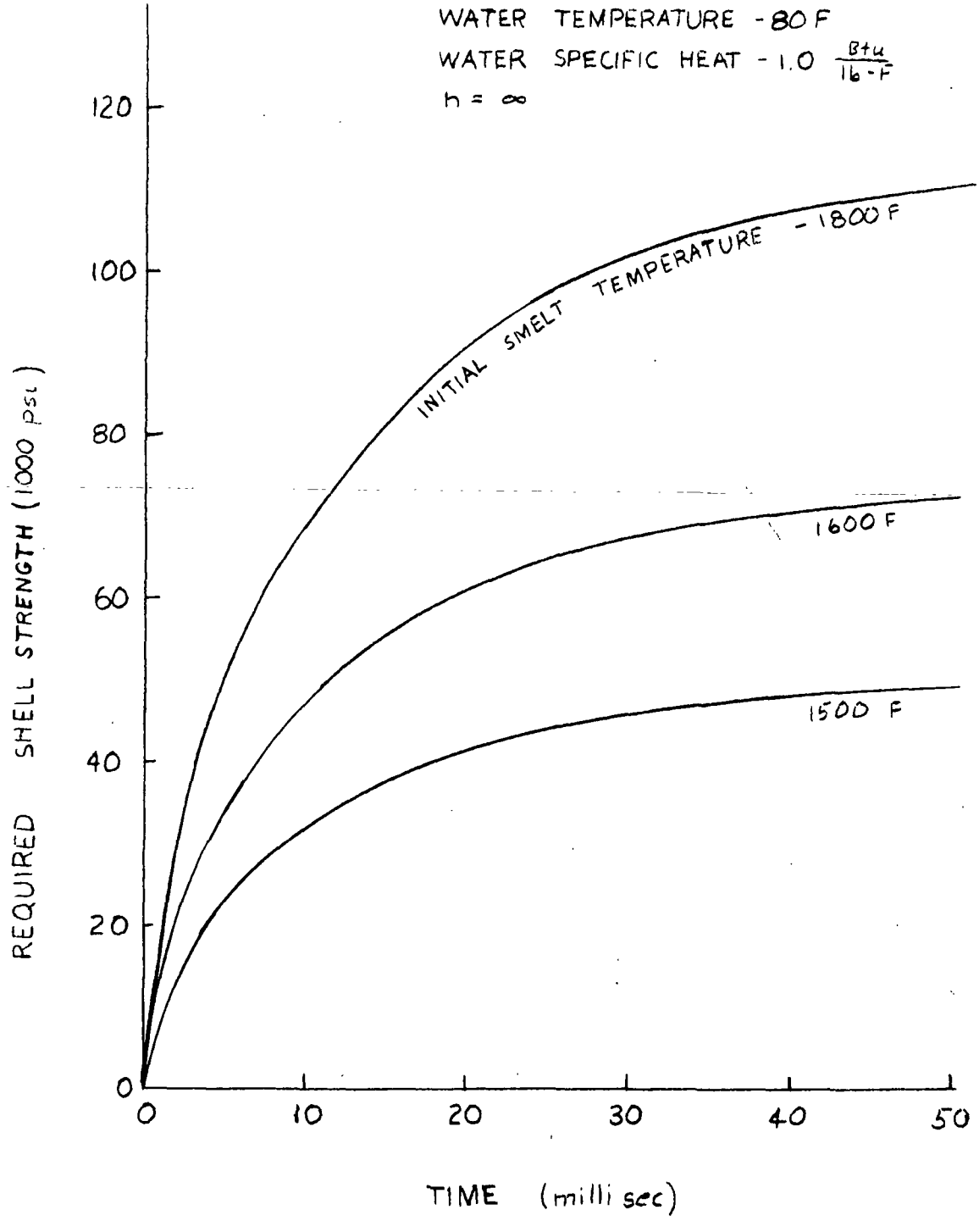


Figure 15

VARIATION OF WATER TEMPERATURE INCREASE WITH TIME FOR VARIOUS VALUES OF SPECIFIC HEAT

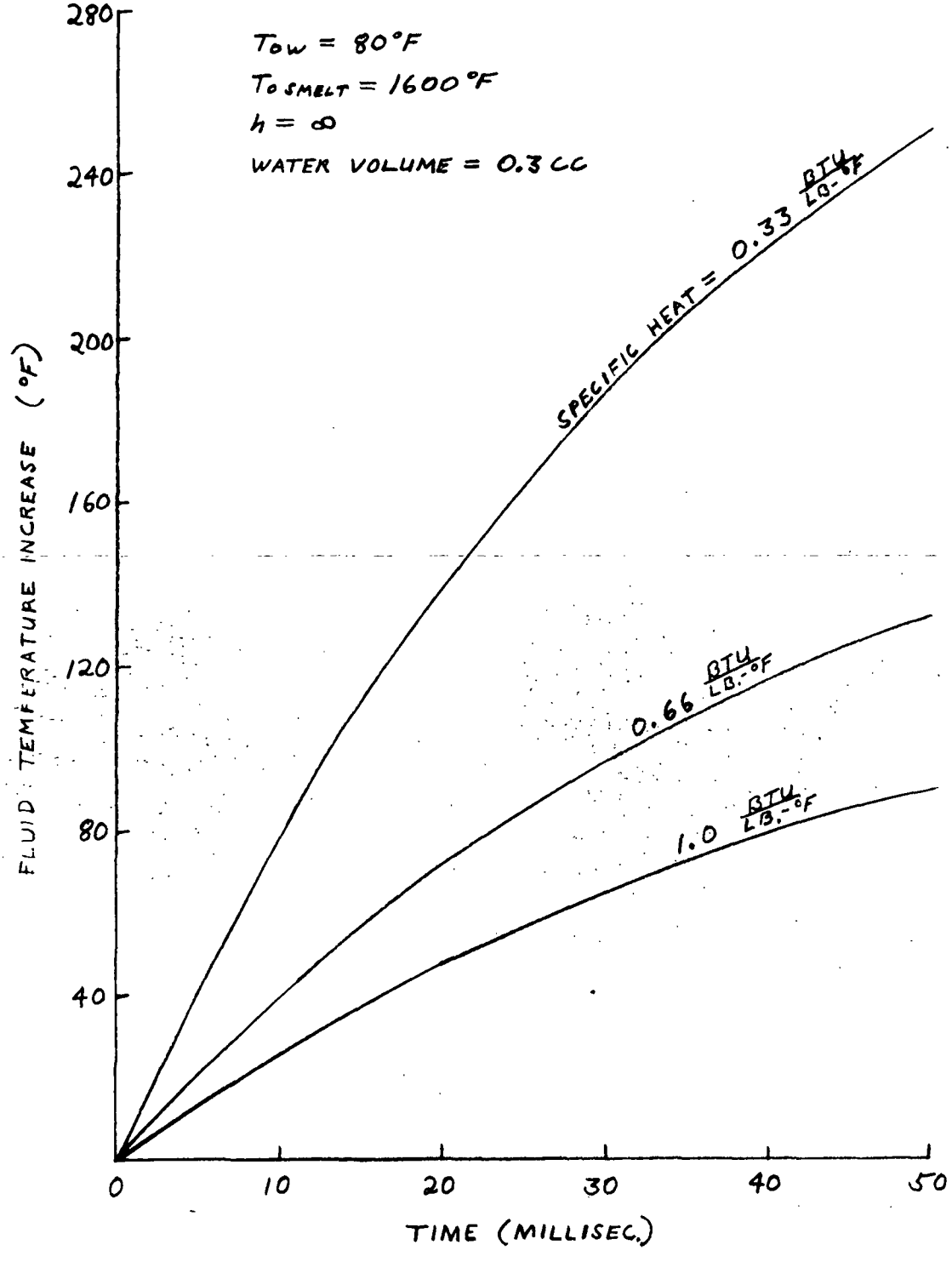


Figure 16

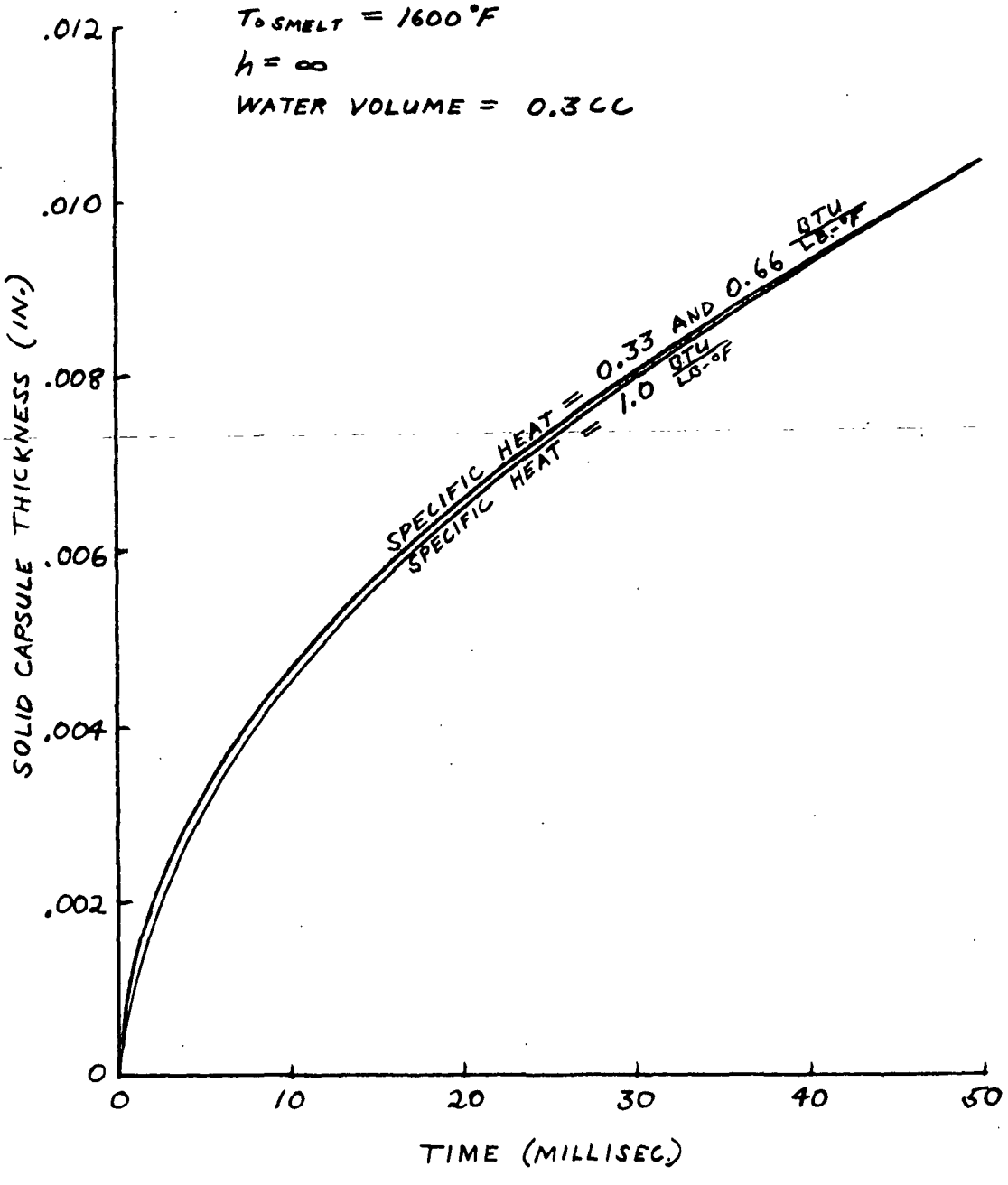
VARIATION OF SOLID CAPSULE THICKNESS WITH TIME FOR VARIOUS VALUES OF SPECIFIC HEAT

$T_{ow} = 80°F$

$T_{o\,SMELT} = 1600°F$

$h = \infty$

WATER VOLUME = 0.3 CC

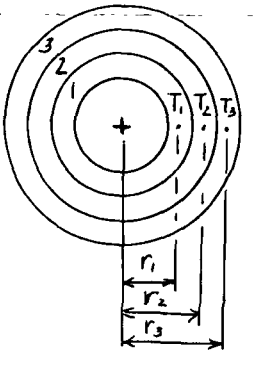


APPENDIX I

CONDUCTION HEAT TRANSFER WITH PHASE CHANGE

When a nucleus having a low temperature is placed in a molten fluid, some of the molten fluid may freeze around the low temperature nucleus. The rate of freezing can be determinedby the conduction heat transfer equation. The nature of the solution of the conduction heat transfer equation for phase change is easily determined for certain cases but, for certain other cases, mathematics does not give a known solution. The encapsulation of a spherical water volume in a molten smelt pool is a case which cannot presently be solved exactly by mathematics. However, the use of numerical analysis or the finite difference approach coupled with a digital computer enables this case to be solved. The nature of the solution is described below.

Consider a series of concentric spherical shells shown below. The thickness of each shell is small enough so that the temperature throughout the shell can be considered constant.



For steady state heat transfer, the amount of heat transfer from one shell to the next for given shell temperatures is given as:

$$Q_{3-2} = \frac{(T_3 - T_2)}{\frac{1}{4\pi k}\left(\frac{1}{r_2} - \frac{1}{r_3}\right)} \qquad (1)$$

A transient heat transfer solution to a conduction problem can be solved by the following approach.

Eq. (1) gives the rate of heat transferred from shell 3 to shell 2. Shell 2 can either transfer this same amount of heat to shell 1 or it can store part or all of the heat. If shell 2 stores part of the heat, its temperature will increase. The temperature increase of shell 2 for a period of time Δt is given as:

$$T_{2,t+\Delta t} - T_{2,t} = \frac{Q_{3-2\ retained}}{\rho_2 V_2 c_2} \Delta t \qquad (2)$$

Where ρ is density, V is volume, c is specific heat, and 2 denotes shell 2.

The temperature increase with time of node 2 is not exactly correct because as T_2 increases, the heat transfer from shell 3 to shell 2 changes. However, if the time interval Δt is small enough, the error of $T_{2,\ t+\Delta t}$ caused by the change of heat transfer is negligible. This gives a method of calculating a transient temperature change of shell 2 for a small time period Δt when the initial temperatures of shell 1, 2 and 3 are known.

The heat transferred from shell 3 to shell 2 is:

$$Q_{3-2} = \frac{T_{3,t} - T_{2,t}}{\frac{1}{4\pi K}\left[\frac{1}{r_2} - \frac{1}{r_3}\right]} \qquad (1)$$

And the heat transferred from shell 2 to shell 1 is:

$$Q_{2-1} = \frac{\left[T_{2,t} - T_{1,t}\right]}{\frac{1}{4\pi K}\left[\frac{1}{r_1} - \frac{1}{r_2}\right]} \qquad (3)$$

The difference between the heat transferred from shell 3 to 2 and from shell 2 to 1 is the heat retained in shell 2 which causes its temperature to rise. The temperature rise of shell 2 is now given as:

$$T_{2,t+\Delta t} = \frac{Q_{3-2,t} - Q_{2-1,t}}{\rho_2 V_2 c_2} \Delta t \qquad (4)$$

or

$$T_{2,t+\Delta t} - T_{2,t} = \frac{1}{\rho_2 V_2 C_2} \left[\frac{(T_{3,t} - T_{2,t})}{\frac{1}{4\pi K}\left(\frac{1}{r_2} - \frac{1}{r_3}\right)} - \frac{(T_{2,t} - T_{1,t})}{\frac{1}{4\pi K}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \right] \Delta t \qquad (5)$$

An equation similar to Eq. 5 can be used to calculate the temperature change for time Δt of shell 1, 3, 4, 5, etc. Also, if the temperatures at time $t+\Delta t$ in Eq. 5 are substituted for the temperatures at time t, the temperatures of the shells can be calculated at time $2\Delta t$. Repeatedly substituting new temperatures into Eq. 5 will give the temperature of shell 2 at any desired time. This type of procedure is well suited to a digital computer.

Now suppose that shell 1 is below a melting temperature and shells 2, 3, 4, 5, etc., are above a melting temperature. The temperature of shell 2 will change until it reaches the melting temperature. When this occurs in nature, shell 2 will begin to solidify and its temperature will remain at the melting temperature until its heat of fusion has been transferred to other shells. The temperature of shell 2 will then continue to change.

The same initial shell temperatures can be used in Eq. 5 to calculate what each shell temperature will be at various times.

Equation 5 will show that the temperature of shell 2 will reach the melting temperature at a given time. When shell 2 reaches this temperature, the melting temperature can be substituted for $T_{2,t}$ in Eq. 5 and temperatures of all shells then calculated without changing $T_{2,t}$. The net amount of heat flowing out of shell 2 is now calculated by Eq. 2 and Eq. 3 and compared with the heat of fusion of shell 2. When the amount of heat flowing out of shell 2 is equal to the heat of fusion, the temperature of shell 2 used in Eq. 5 is again allowed to vary with time. This gives a solution to the transient conduction heat transfer equation with a phase change for any desired case.

The solution described above is for spherical shells, but works equally well for plane slabs and concentric cylinders. This gives a means of checking the accuracy of the solution. An exact solution is known for the case of a plane slab exposed to a boundary maintained at zero temperature. The approximate solution described above can be used for the same conditions. To do this, slab 1 is given a very large specific heat which will make its temperature variation negligible. Its initial temperature is then specified as zero and the initial temperatures of slabs 2, 3, 4, etc., are specified at some value above the melting temperature. The temperature change with time of each slab is calculated with an equation similar to Eq. 5 and these temperatures can be compared with the exact solution for the same conditions. Such a comparison is shown in Figure A1. Figure A1 shows that the temperature calculated for the time at which a slab just reaches the melting temperature agree with the exact solution. However, as the temperature of that slab is held constant, the amount of error increases due to the finite thickness of the slab. This indicates that the calculated temperatures used should be those given for the time when a slab just reaches its melting temperature.

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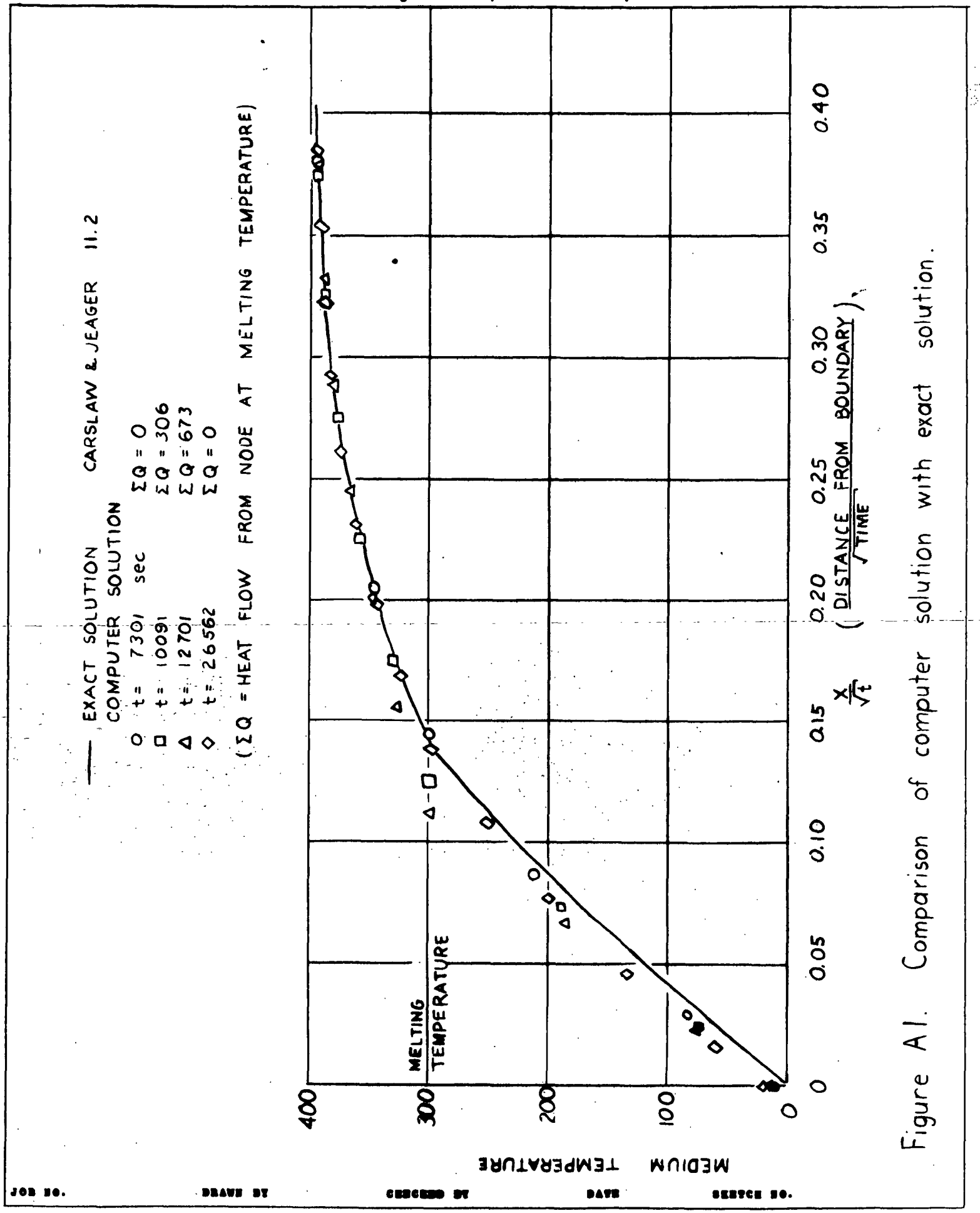

Figure A1. Comparison of computer solution with exact solution.

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